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PAPERS ACCEPTED FOR PUBLICATION:

On the Determination of Fat and Casein in Feces. By Herman Poole.

The Electrolytic Determination of Cadmium. By Daniel L. Wallace and Edgar F. Smith.

A Comparison of Various Methods of Determining Carbon Dioxide and Carbon Monoxide. By L. M. Dennis and C. G. Edgar.

On the Reaction between Mercury and Concentrated Sulphuric Acid. By Chas. Baskerville and F. W. Miller.

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THE JOURNAL

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NOTES ON SELENIUM AND TELLURIUM.

BY EDWARD KELLER.

Received July 30, 1897.

IT is not very frequently that the technical chemist and the assayer, or the metallurgist, meet with the two elements, selenium and tellurium, although the assayer's work in gold assaying and treatment of the ores is often rendered more difficult by their presence. No analysis of any of the western, crude copper, however, is now complete without the joint, or separate, determination of selenium and tellurium.

It is not the object of this paper to fully describe any of the methods in use for their separation from other elements. A few new features, merely, will be pointed out.

It has long been known that many acid-forming elements are precipitated by ferric hydroxide as insoluble salts, from ammoniacal solution.

To have introduced this principle into copper analysis is entirely the merit of present and former chemists of the Baltimore Copper Smelting and Rolling Co.—the Messrs. Lehmann, Mager, and Johns.[1]

The elements of this group which occur, or may occur, in copper are phosphorus, arsenic, antimony, tin, selenium, and tellurium.[2] With all these elements this method may be most successfully employed when they are present in small quantity and the precipitation of the copper becomes impracticable.

[1] Lehmann and Mager: *Am. Chem. J.*, July, 1885.

[2] Cabell Whitehead: This Journal, 17, 280.

When the proper conditions are observed it is most efficient, rapid, and simple. From five to many hundred grams of copper, with a comparatively very small amount of iron, are dissolved in nitric acid, enough ammonia added to hold all copper in solution, boiled, and the ferric hydroxide filtered and washed.

From this precipitate the enumerated elements can easily be separated by known methods.

The following is illustrative of the behavior of selenium and tellurium in relation to this ferric hydroxide separation method. Of each element one gram was taken, and by oxidation with dilute nitric acid a solution of selenous and one of tellurous acid obtained. One gram of ferrous sulphate was dissolved and oxidized, and that amount of iron added to each solution, as well as to each succeeding filtrate (previously acidified) after the ferric hydroxide, precipitated by ammonia, was collected on a filter and washed. The ferric hydroxide precipitates were each dissolved in hydrochloric acid of the proper strength, and the selenium precipitated with ferrous sulphate, the tellurium with sulphur dioxide, and determined on tared filters.

The quantitative results were as follows:

Element.	Quantity taken.	No. of precipitations.									Quantity found.
		1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	
	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram
Se..	1	0.0892	0.0973	0.1546	0.1297	0.2219	0.1416	0.1236	0.0513	0.0121	0	1.0213
Te..	1	0.9548	0.0448	0	....	....	....	....	....	....	....	0.9996

It is clear that the reaction is quantitative only when a certain excess of iron is present, which for selenium must be many times greater than for tellurium.

The method universally recommended for the separation of selenium and tellurium is the potassium cyanide method, selenium being readily soluble in a solution of that compound. Tellurium is also dissolved in small quantities, which must be again separated, and for that reason the method is unsatisfactory.

The best precipitant for both elements is declared to be sulphur dioxide.

To obtain the metallic precipitates by any reducing agents the two elements must be in solution as selenous and tellurous acids. The same is true if the sulphides are desired by precipi-

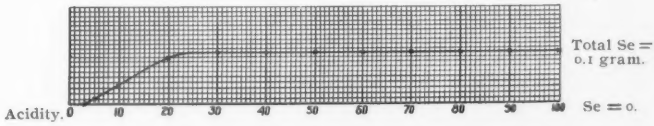
tation with hydrogen sulphide. Selenic and telluric acids are only reduced to the lower form by strong boiling hydrochloric acid. In describing the experiments made, the solutions spoken of are always those of the former acids.

In the reaction of selenous and tellurous acids with sulphur dioxide the two show characteristic differences. When precipitated by that gas no heavy metals must be present, since they are also, at least partially, precipitated.

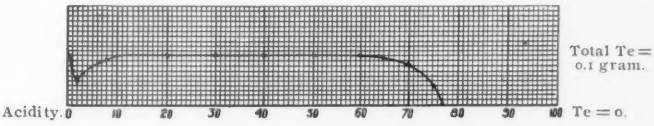
Example.—With one-half gram of copper and 0.1726 gram of selenium in solution, 0.0865 gram of copper was thrown down.

In the following determinations, the acid of which the percentage is given is strong hydrochloric of the specific gravity 1.175. The amount of selenium and tellurium in each case is

PRECIPITATION OF SELENIUM BY SULPHUR DIOXIDE.



PRECIPITATION OF TELLURIUM BY SULPHUR DIOXIDE.



one-tenth gram. The sulphur dioxide passed through the solution until thorough saturation. Time of standing about twenty hours. The reaction was conducted in the cold.

PRECIPITATION OF SELENIUM AND TELLURIUM BY SULPHUR DIOXIDE.

	Percentage of acidity of solution.								
Precipitation of	0.5	1	2	3	5	8	10	20	
Selenium ...	....	0	....	trace	0.0124	....	0.0349	0.0935	
Tellurium ...	total	0.0761	0.0525	0.0653	0.0745	0.0931	total	total	

	Percentage of acidity of solution.									
Precipitation of	30	40	50	60	65	70	75	80	90	100
Selenium	total	total	total	total	total	total	total	total	total	total
Tellurium	total	total	total	total	0.0965	0.0882	0.0411	0	0	0

The accompanying graphical representation of these figures perhaps conveys a more clear idea of the difference of behavior of the two elements.

From the above facts we learn that even with sulphur dioxide in a hydrochloric acid solution of over eighty per cent. acid a separation is possible. We also see that to obtain a total precipitation of the two elements together in this way, the acidity must be confined to definite limits, safely between thirty and fifty per cent.; otherwise one or the other of the two will remain wholly or partially in solution.

If, after saturation with sulphur dioxide, of a selenous acid solution of insufficient acidity, the necessary amount of hydrochloric acid be added, the precipitation becomes total. The same is the case with tellurium in case of insufficient acidity. In case of too high acidity, diluting to the required strength calls forth total precipitation.

The figures for partial precipitation are not absolutely constant. They show variations under different conditions, such as temperature and time of exposure to the action of the reducing agents.

Both elements are more voluminous when precipitated from weak acid solutions than when precipitated from stronger ones.

Ferrous sulphate does not precipitate tellurium.

A series of determinations of selenium, precipitated from solutions of various acidity by ferrous sulphate, showed that the reaction is rapid and quantitative in strong hydrochloric acid. The degree of rapidity of precipitation diminishes as the acidity is reduced. It is total within twenty-four hours as long as the acid is thirty per cent. or more. In fact the reactions of ferrous sulphate and selenous acid are almost identical with those of that acid and sulphur dioxide.

These facts furnish a simple method to separate selenium from tellurium, or any other of the ordinary elements, for analytical or industrial purposes. Gold and silver only, of the metals usually present, interfere. Gold may previously be precipitated by oxalic acid, which does not affect selenium, and silver is so readily separated as chloride that it is no obstacle. Or gold may be precipitated with the selenium and weighed together and the latter dissolved with nitric acid, leaving the gold in

weighable form. Selenium is then obtained by difference.

In attempting to make electrolytic copper determinations in copper residues (from electrolytic tanks), these were treated with strong nitric acid, the silver precipitated as chloride, and filtered. The filtrate, now being freed from gold, silver, and much antimony, was then evaporated to dryness and the residue boiled with hydrochloric acid until the nitrates were fully decomposed. The excess of acid was next neutralized with ammonia, and into the slightly acid solution was conducted hydrogen sulphide. The precipitate, after filtering and washing, was digested with a sodium sulphide solution, and after again filtering and washing, redissolved in nitric acid, made ammoniacal and, for the purpose of precipitating lead and bismuth, ammonium carbonate and phosphate added, and boiled. After cooling and filtering, the ammoniacal copper solution was acidified with sulphuric acid and subjected to electrolysis. It was thought to have been freed of all deleterious elements. The precipitate of copper, however, failed to come down bright and thoroughly adhesive, and on solution with somewhat diluted nitric acid a reddish residue would be visible on the cathode. This proved to be selenium.

The selenium in the same residues was then separated and it was found, by a number of quantitative determinations, that by precipitation with hydrogen sulphide, and subsequent treatment with sodium sulphide, from two-thirds to seven-eighths of the selenium was retained by the insoluble sulphides of copper, bismuth, and lead, the remainder being in the sodium sulphide solution, the latter always containing all of the tellurium.

Looking over many text-books and considerable original literature, I found only one allusion to this fact. William Crookes in his Select Methods in Chemical Analysis, p. 426, *1894*, says: "Selenium cannot be separated from metals with which it is combined when the sulphides of these metals are insoluble in ammonium sulphide, by making use of the solubility of selenium in this reagent. The insoluble metallic sulphide is almost always mixed with selenide."

Here it should be remembered that the precipitation of selenium, as selenium sulphide, SeS_2, from a solution of selenous

acid with hydrogen sulphide, should be conducted in the cold. The precipitate has then a lemon-yellow color and is very readily dissolved by the alkaline sulphide solutions. On heating, this yellow precipitate darkens to an orange color and becomes insoluble. This is said to be due to decomposition and the insolubility of selenium.

Ditte[1] tells us that when selenium and sulphur combine, in the above-mentioned manner, heat is absorbed, or the heat of formation is negative. This sulphide, like hydrogen iodide, belongs, therefore, to a class of compounds which readily decompose.

After a number of qualitative tests, demonstrating that copper, bismuth, and lead, separately retain selenium, to a greater or less extent, according to conditions, the following quantitative determinations were made :

The quantity of selenium in each case was about two grams. This and the varying quantities of copper were in hydrochloric acid solution, with just enough free acid to prevent any precipitation of copper selenite. The precipitation with hydrogen sulphide was conducted under cooling and the resulting precipitate washed with cold water, digested with a strong solution of sodium sulphide, then washed with water containing a few drops of the same reagent, then with water to which a little ammonium sulphide was added, and finally with strong alcohol. Sulphur, selenium, and copper were then determined in the precipitate. The results are given in the table below :

	I. Gram.	II. Gram.	III. Gram.	IV. Gram.
Sulphur	0.3787	0.1649	0.1730	0.0416
Selenium	0.2828	0.1726	0.1565	0.0239
Copper.....	0.9880	0.4880	0.4909	0.0979

Figuring the theoretical amount of copper, as combined with the sulphur and selenium found, we obtain :

	I. Gram.	II. Gram.	III. Gram.	IV. Gram.
Cu combined with S.....	0.7503	0.3267	0.3428	0.0824
Cu " " Se.....	0.2263	0.1385	0.1256	0.0192
Total.....	0.9766	0.4652	0.4684	0.1016

[1] *Ann. Chem. Pharm.*, 163, 187.

In another experiment selenium and copper were subjected to the action of hydrogen sulphide in ammoniacal solution, and the precipitate treated as those previously described. The results obtained were:

	Gram.
Sulphur	0.0098
Selenium	0.0138
Copper	0.0231
Copper (theoretical)	Gram.
Combined with sulphur	0.0163
" " selenium	0.0111
Total	0.0274

The initial amount of copper in this last case was 0.05 gram, and, as was expected, a large portion remained in the ammonium sulphide solution.

While the results do not appear very satisfactory from the standpoint of analytical accuracy, it should be stated that the purpose of the determinations was to find the existence or non-existence of a definite reaction, and the molecular proportions of the sulphide and selenide formed. At first sight the results might be considered of a negative character. On closer observation, however, two out of the first four determinations show a maximum of selenide, or a minimum of sulphide formation, in which the atomic ratio of selenium and sulphur is approximately 1 : 2, or the same as in selenium sulphide, as formed by the reaction of selenous acid and hydrogen sulphide.

$$SeO_2 + 2H_2S = SeS_2 + 2H_2O.$$

By the precipitation in ammoniacal solution the contents of selenium in the precipitate are higher. It is quite likely, however, that in this case more of the copper sulphide than of the selenide was held in solution by the ammonium sulphide, and it is clear that in acid, as well as in alkaline, solution only a certain maximum quantity of copper selenide is formed which never equals the amount (molecularly) of copper sulphide.

According to the above it may plausibly be supposed that the reaction takes place in two stages:

I. $SeO_2 + 2H_2S = SeS_2 + 2H_2O.$

II. $3CuCl_2 + SeS_2 + 3H_2S = 2CuS + CuSe + 6HCl + 3S.$

For this theory there is no positive proof; but it is plain that the hydrogen sulphide must reduce both copper chloride and selenous acid, that copper and selenium may combine in their nascent state, and that sulphur is precipitated, or that copper may combine with previously formed selenium sulphide, and that this also must be accompanied by sulphur precipitation.

The reaction appears one of the most interesting in inorganic chemistry and deserves further investigation.

BALTIMORE COPPER WORKS, July, 1897.

COMPOSITION AND FORMATION OF TANK RESIDUES IN ELECTROLYTIC COPPER REFINERIES.

BY EDWARD KELLER.

Received July 30, 1897.

THE production of electrolytic copper and its separation of other metals by means of the electric current, was first established on a commercial scale by James B. Elkington, of England. In two patents, No. 2,838, Nov. 3, 1865, and No. 3,120, Oct. 27, 1869, he laid down all the essential points of the processes which guide the operations at the present day.

The original object of the process was mainly the separation of the precious metals from the copper. The production of a pure copper from the crude metal is, however, now equally important. The process may be described briefly as follows: The crude copper is cast into anodes of generally six to eight square feet by one to one and one-half inches in thickness. These are suspended in tanks, alternating with thin sheets of pure copper, as cathodes, one to two inches apart. Of the cathodes there is one more in number than of the anodes. In the tanks the electrolyte, in which anodes and cathodes are submerged, is forced to circulate in order to maintain uniform density. This electrolyte is said to be generally a solution of three per cent. copper (as sulphate) with six per cent. of free sulphuric acid.

Each anode is connected with the conductor from the positive pole of the dynamo, each cathode with the negative. If the number of anodes in one tank be n, we have n branches of the electric current from the positive pole, and $n+1$ from the negative. Anodes and cathodes being otherwise insulated, the current must pass from anode through the electrolyte to cathode,

dissolving the copper of the former and depositing it on the latter. The same current passes through a series of tanks, which may number many hundred.

The system described is called the "multiple." The "series" system is a later invention. It differs from the former, that in each tank there is at one end but one anode connected with the positive pole, and at the opposite end but one cathode with the negative. The space between is filled with rolled copper plates, set vertically, all a certain distance from each other. Electrolyte and circulation are the same as in the other system. When the electric current passes through this system, each surface of the individual plates facing the anode becomes a cathode surface, and that facing the cathode becomes an anode surface, so that the copper dissolved on the anode surface of each plate is deposited on the opposite, or cathode surface of the next plate.

Details of the series system, with illustrations, may be seen in the papers of United States patents No. 377,487, Feb. 7, 1888, and No. 459,838, Sept. 22, 1891, secured by Mr. Edward S. Hayden, of Waterbury, Conn.

The precious metals and part of the impurities of the dissolved anodes, in either system, fall to the bottom of the tanks, forming there a sediment or residue, frequently also called slimes, mud, etc.

It is the object of this paper to show how some of these latter products are composed and to what extent the various impurities in the anode copper take part in their formation.

In the following are given partial analyses (oxygen and hydrate water were not determined) of residues from copper derived from ores from Butte, Mont., as also the composition of the corresponding anode copper. The copper of I was made by the reverberatory, of II by the converter process:

I.

	Residues.		Anode copper.
Ag....	53.894 per cent.	= 15718.7 ozs.	100.1 ozs.
Au...	0.2959 " "	= 86.3 "	
Cu....	11.010 " "		
Pb....	0.910 " "		0.0093 per cent.
Bi.....	3.930 " "		0.0320 " "
Sb	6.250 " "		0.0651 " "
As	2.107 " "		0.0586 " "
Se	0.394 " "	Se and Te..	0.0098 " "

	Residues.		Anode copper.
Te	1.174	per cent.	
SO_4 ...	5.268	" "	
H_2O[1] ..	2.365	" "	

II.

	Residues.		Anode copper.
Ag....	55.150 per cent.	= 16085.04 ozs.	100.47 ozs.
Au....	0.198 " "	= 57.749 "	
Cu	13.820 " "		
Pb	2.070 " "		
Bi	0.340 " "		0.0035 per cent.
Sb	2.440 " "		0.0510 " "
As	1.090 " "		0.0180 " "
Se.....	0.718 " "		
Te	0.892 " "		
Fe	0.800 " "		
SO_4 ...	10.680 " "		
H_2O...	2.604 " "		

The figures in I represent the average of nearly a one year's run; in II a three months' run in the same refinery.

In the formation of these residues the anodes contribute all their contents in silver, gold, selenium, and tellurium. From any one of these elements we are, therefore, enabled to compute their degree of concentration in the residues, and to figure the amount of partial deposition therein of the other elements.

Since silver constitutes by far the greatest quantity, and consequently its determination being the most accurate, it is best to proceed from it. We then have:

I.

	Residues. Ounces.	Anode copper. Ounces.	Concentration.
Ag	15718.7	100.1	157

II.

	Residues. Ounces.	Anode copper. Ounces.	Concentration.
Ag	16085.05	100.47	160

Dividing the percentages in residues of partially deposited elements by the figures for concentration, we obtain the percentages of the original quantity in the anodes deposited in the residues. The difference between this and the total contents in the anodes is the amount gone into solution in the electrolyte.

[1] The sample was dried at the temperature of boiling water and the remaining water determined at 250° C.

From the latter, practically all the copper dissolved from the anode is deposited on the cathode, carrying with it but a few per cent. of the impurities in solution.

Proceeding according to the above, we obtain the following:

I.

	Contents of anodes.	Amount of original contents in anodes gone into residue and solution. In residue.	In solution.
	Per cent.	Per cent.	Per cent.
Cu	99.3	0.07	99.93
Bi	0.0320	78.22	21.78
Sb	0.0651	61.14	38.86
As	0.0586	22.90	77.10

II.

	Per cent.	Per cent.	Per cent.
Cu	99.4	0.086	99.914
Bi	0.0035	60.71	39.29
Sb	0.0510	29.90	70.10
As	0.0180	37.84	62.16

Lead is not considered in these figures, because lead-lined tanks and lead sulphate, carried by the commercial sulphuric acid employed, render the obtaining of correct results impossible.

There is little similarity between the compositions of I and II. In I the quantities of bismuth, antimony, and arsenic in the anodes are not very widely different. Bismuth shows the least solubility, arsenic the greatest. In II, where antimony greatly preponderates in the anodes, that element also shows the greatest solubility.

The ratio of selenium and tellurium in the two samples of residues may be worthy of notice. We have for I, 1 : 3; for II, 7 : 9. The current opinion, that selenium is merely a minor companion-element to tellurium in our western copper, seems thereby proven to be erroneous.

The ratio of the two elements in the anode copper is without doubt the same, and as they have never been separated from copper for quantitative determination individually, it can readily be shown by dividing their percentages in the residues by the figure of concentration what their quantities are in the corresponding anodes. We find:

IN ANODES.

	I. Per cent.	II. Per cent.
Se	0.00251	0.00449
Te	0.00748	0.00558
Total	0.00999	0.01007

The total of the two elements thus calculated, 0.0999 per cent., for I, corresponds closely with the actual amount, 0.0098 per cent., found in the anodes. For II no direct determination was made in the anodes.

BALTIMORE COPPER WORKS, July, 1897.

SOME PRODUCTS OF THE TUBERCULOSIS BACILLUS.

BY E. A. DE SCHWEINITZ AND MARION DORSET.

Received June 17, 1897.

TUBERCULIN, as is well known, is the extract of the tuberculosis bacilli, including the media upon which they are grown. From specially prepared artificial cultures of the tuberculosis germ, Kühne and independently one of us,[1] obtained a substance corresponding to a nucleo-albumin, which appears to be the fever-producing principle of the germ. However, many conditions in tuberculosis were not accounted for by this substance, and as Mafucci, Prudden and Hodenpeyl, Vissman, and others, had succeeded in producing tubercular nodules without necrosis by the intravenous injection of dead bacilli, it seemed as though it should be possible to isolate either from cultures or from bodies of the germs themselves, some substance which might be considered accountable for the coagulation necrosis of tissue which takes place, a necrosis which appears necessary for the progress of the disease. This problem was undertaken by my assistant, Dr. Dorset, and myself more than two years ago. After many fruitless attempts we succeeded in isolating from artificial cultures a crystalline substance, having a melting-point of 161°–164° C., readily soluble in ether, alcohol, and water, which separated from these solutions in needle-like or prismatic crystals, showing a slight yellow tint. They did not give the biuret reaction. The solution of this substance has an acid reaction to litmus, is acid in taste, and is optically inactive. The crystals give no precipitate with silver nitrate, platinic chloride, or barium hydroxide. The analy-

[1] DE SCHWEINITZ: Bulletin No. 7, Bureau of Animal Industry.

sis showed carbon 50.88 per cent., hydrogen 6.70 per cent., oxygen 43.42 per cent., giving a formula corresponding closely to $C_7H_{10}O_4$. This is the formula of teraconic acid, an unsaturated acid of the fatty series.

The culture media upon which the germs were grown and from which these crystals were obtained, contained potassium acid phosphate, ammonium phosphate, asparagin, or the solution of these salts without asparagin, and glycerol, the medium used by one of us (de Schweinitz)[1] some years ago for studying these germs. After the germs have been growing on this medium for some weeks the liquid becomes light yellow in color, having the appearance of a pale urine, a change which does not take place in the uninoculated medium kept under the same conditions. Efforts to obtain this same acid from the ordinary beef broth cultures containing peptone and glycerol resulted in securing minute amounts of the crystals only, which it was never possible to purify. After noting some of the other properties of this acid substance we came to the conclusion that the presence of peptone and the nitrogenous bases of the meat resulted in their combination with the crystals forming compounds from which the acid could not again be easily extracted, even after the addition of acid. Finally, a small quantity of the crystalline substance obtained from the artificial cultures was added to the glycerol peptonized beef broth medium, but it was impossible to recover it again by the methods used for the first extraction, *viz.*, repeated precipitation with alcohol, solution in water and extraction with ether. The ready solubility of this substance in water, as well as ether, probably accounts for the difficulty of obtaining it. The uninoculated medium did not yield these crystals. When dissolved in water and injected into guinea pigs, this substance caused a reduction of temperature and necrosis of the areas with which it came in contact. As this had been observed in a number of experiments, the idea was suggested that this acid, evidently a secretion of the germ, was one of its most powerful weapons, that by its action upon the tissue the cells were first destroyed so that they could subsequently be utilized by the germ as food, and in this way the germ protected itself from surrounding leucocytes. To test this, crystals dis-

[1] *New York Medical Journal*, 1893.

solved in sterile water were injected by means of a hypodermic syringe directly into the liver tissue of a guinea pig. At the same time the same quantity of water was injected into a check in the same way. After forty-eight hours, check and experimental animals were killed. The check failed to show any effect, while the others exhibited a liver with several light spots and necrotic areas. Repetition of this experiment gave the same results.

No effort was made to recover these crystals from the liver as the amount used was too small. As the growth of the tuberculosis bacillus in the body is localized and where localized the necrotic areas are apparent, the fairest test was to bring the substance as soon as possible in contact with the liver tissue.

It seems very reasonable to conclude that we have here the substance formed by the tuberculosis germ, which is responsible for the coagulation necrosis in this disease. The formula which can be deduced from the analysis makes this acid correspond closely to teraconic, which has properties very similar to those noted by us in connection with this new acid. Its identity we have not yet proved or disproved. The amount of this acid obtainable is very small, so that we have used only a very small portion of it for testing its immunizing property. A single injection of 0.0029 gram was sufficient to keep the animals alive some weeks longer than the checks, and its solution appeared to exert some slight bactericidal influence.

As this substance seemed to be a temperature-reducing principle in healthy and diseased animals, we endeavored to separate from tuberculosis cultures the fever-producing principle. The crystals were always found in the culture liquid and only minute amounts could be obtained from the germs themselves that had been grown on liquid media. Accordingly, these germs carefully filtered without heat, were washed with cold water and next extracted with hot water. This hot water extract contained an albuminoid which caused the tuberculin reaction in tuberculous guinea pigs and calves upon repeated injections.

Roux and Nocard claim that they have a tuberculin which will give reactions almost indefinitely, but do not describe its method of preparation. Whether this is the same substance that we have obtained we are unable to say, but certain it is that the tuberculin prepared in the way we have indicated will

give reactions four or five times in succession where the reaction with tuberculin, as prepared in the ordinary way, fails after the second time. The conclusion is a fair one, we think, that the fever-reducing principle having been removed to an extent, if not entirely, the immunity to the fever-producing principle is much more slowly acquired. In the *Deut. Med. Wochen*, April 1, 1897, Dr. R. Koch describes some new tuberculin preparations. The dried tuberculosis bacilli were taken (the culture medium used is not mentioned), finely powdered, and centrifugalized with distilled water. The opalescent solution obtained tested upon animals gave the tuberculin reaction. The residual germs were submitted to this treatment a number of times until finally all were practically dissolved. The latter solutions, he said, in large doses caused a reaction, but in small quantities did not produce this result, and seemed to exert both an immunizing and curative action in experimental tuberculosis. Koch used for this work virulent germs and claims that attenuated germs do not give an active product. Our work was done with germs purposely attenuated by cultivation and the results show that a very active fever-producing, fever-reducing, and probably curative principle can be obtained from them. It hardly seemed justifiable to ourselves to powder dried virulent germs and have the dust floating in the air. Koch further refers to two fatty acids, which, in conjunction with Proskauer, had been found in the bodies of the germs. The writers of this paper published in this Journal, August, 1895, a preliminary study of the fats of the tuberculosis bacilli, showing the high content of the fat in the body of these germs, which accounts for the difficulty in staining them with certain colors, as well as their difficult absorption. In a later paper[1] we described briefly the different acids obtained from these fats, both high-melting and low-melting. Whether these are identical with the acids referred to by Koch we are unable to say, from the brief description he has so far given. This interesting necrotic acid, which plays so important a part apparently in the progress of tuberculosis, and the fever-producing principle formed by the tuberculosis germ are receiving further chemical study. Their physiological importance is very great. The acid may be tentatively called tuberculinic acid.

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[1] *Centrbl. Bak. u. Parasit.*, **19**, 18, 19, 707.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, UNIVERSITY OF MICHIGAN.]

FURTHER STUDY ON THE INFLUENCE OF HEAT TREATMENT AND CARBON UPON THE SOLUBILITY OF PHOSPHORUS IN STEEL.

BY E. D. CAMPBELL AND S. C. BABCOCK.

Received June 29, 1897.

ABOUT a year ago we published a paper upon the same subject as that of the present research.[1] At the time of our previous work we did not have a pyrometer on which we could depend, so that we were unable to state with accuracy the exact treatment to which the material under examination had been subjected. Since the time of our previous work we have obtained an accurate Le Chatelier pyrometer so that we have been able to heat specimens up to 1,100°, with probable error of not over 5°.

The heat treatment to which the specimens in the table given below were subjected are as follows: The metal called "annealed" was raised to between 900° and 1,000° and then allowed to cool slowly. The specimens called "quenched from $x°$" were placed in a porcelain-lined iron tube with the thermal junction of the Le Chatelier pyrometer in contact with the specimen. The portion of the tube containing the specimen was slowly heated by means of a Hoskins' Gasolene Furnace until the desired temperature was reached. The time required for heating the specimens was usually from twenty-five to forty minutes. When the desired temperature was reached, the tube was tilted up so that the specimen dropped directly into ice-water at a temperature of from 4° to 5°. The specimens so prepared were then either drilled or pounded sufficiently fine to enable them to be used for chemical examination.

The method of analysis employed is somewhat different from that described in our previous paper. Instead of treating first with neutral mercuric chloride, then after filtering and washing the precipitated mercury, treating this latter with four per cent. hydrochloric acid, and finally volatilizing the mercury and determining the phosphorus in the residue, we have shortened the

[1] *Am. Chem. J.*, **18**, 719.

process and determined only the phosphorus soluble in a slightly acid solution of mercuric chloride. The objections to the process employed last year are principally, the length of time necessary for handling the precipitates, and to a less extent the fact that the amount of phosphorus soluble in hydrochloric acid increases somewhat with the time of digestion, thus necessitating the adoption of an empirical length of time of treatment with the reagent. In the method which we have employed in the present work, we have demonstrated by numerous experiments that the length of time of standing has no appreciable effect on the solubility of the phosphorus in a given sample. A specimen digested one and one-half hours gave 0.096 per cent. soluble, while another sample of the same specimen gave 0.093 per cent. after standing forty hours.

The special solutions employed in the determination of the soluble phosphorus were as follows: The 'two per cent. hydrochloric' is twenty cc. hydrochloric acid (sp. gr. 1.20) made up to one liter. The ferric chloride solution is 8.15 grams of iron wire containing 0.050 per cent. phosphorus dissolved in 1.20 nitric acid, boiled, and evaporated to dryness with excess of hydrochloric acid, sufficient to convert it to ferric chloride. After evaporation to dryness the ferric chloride was taken up with twenty-five cc. hydrochloric acid, transferred to a 250 cc. flask, and made up to the mark. Five cc. of this solution contains five-tenths cc. of free hydrochloric acid and sufficient phosphorus to give five milligrams precipitate of ammonium phosphomolybdate, which amount was deducted from the weight of the precipitates obtained in the course of the work. The ammonium acetate solution was made by dissolving 400 grams of ammonium acetate in 800 cc. of water.

The method employed is as follows: Five grams of the steel is introduced into an Erlenmeyer flask and thirty-five grams of powdered mercuric chloride added; to this is further added 100 cc. of two per cent. hydrochloric acid and the flask tightly stoppered. The whole is allowed to stand, with occasional shaking, for one and one-half hours, or until solution is complete. The solution is then filtered by aid of a pump and the precipitated mercury washed four times with hot water. A convenient method for filtering and washing the precipitated mercury is to

employ a perforated porcelain disk about four cm. in diameter, held in a funnel. On this is placed one filter paper just the size of the disk, and a second one on top being slightly larger. After fitting the upper one by wetting and pressing down firmly a small amount of finely divided asbestos, suspended in water, may be poured on, which will serve to make the points tight and facilitate the removal of the paper and mercury after washing.

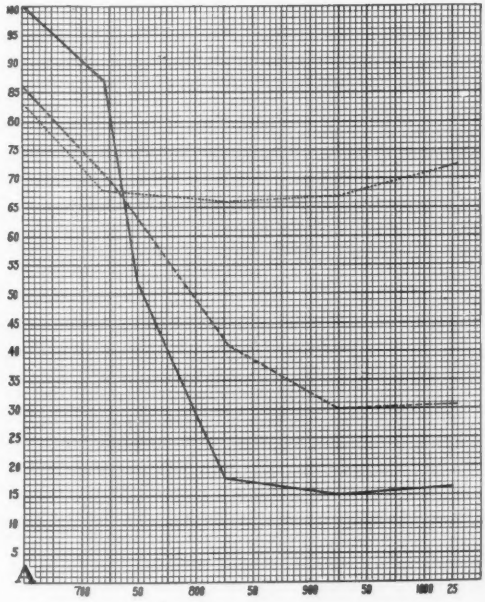
To the filtrate and washings from the precipitated mercury, amounting to 200 to 225 cc., is added five cc. of the ferric chloride solution and fifteen cc. of the ammonium acetate. The whole is then covered in lipless beakers and brought almost to a boil, when the basic acetate carrying ferric phosphate is precipitated. The solution is then filtered and allowed to drain without washing. The filter containing the basic acetate is transferred to the beaker in which the precipitation was made and heated with twenty cc. of strong nitric acid until the solution is complete. After diluting with twice its volume of water, the filter paper is filtered out and washed with hot water, acidified with nitric acid, and the solution boiled down and the phosphorus precipitated with ammonium molybdate. From the weight of the ammonium phosphomolybdate weighed on asbestos funnels, dried at 120°, is deducted five milligrams for the phosphorus contained in the ferric chloride solution used, and the per cent. of the phosphorus soluble is then calculated.

The results obtained on three specimens of steel are given in the following table:

Name of steel.	Chemical composition. C.	P.	Mn.	S.	Si.	Heat treatment.	Quenching temperature.	Per cent. of phosphor's soluble in acid $HgCl_2$	Per cent. of total phosphorus soluble in acid $HgCl_2$.
Cl 5	0.10	0.119	0.484	....	....	annealed	....	0.099	83.2
Cl 5	0.10	0.119	0.484	....	....		719°	0.081	68.08
Cl 5	0.10	0.119	0.484	....	....		825°	0.079	66.4
Cl 5	0.10	0.119	0.484	....	....		928°	0.080	67.2
Cl 5	0.10	0.119	0.484	....	....		1028°	0.086	72.2
N.S. 5	0.37	0.160	0.820	....	....	annealed	....	0.137	85.6
N.S. 5	0.37	0.160	0.820	....	....		728°	0.110	68.8
N.S. 5	0.37	0.160	0.820	....	....		827°	0.066	41.2
N.S. 5	0.37	0.160	0.820	....	....		923°	0.048	30.0
N.S. 5	0.37	0.160	0.820	....	....		1027°	0.049	30.6

Name of steel.	Chemical composition. C.	P.	Mn.	S.	Si.	Heat treatment. Quenching temperature.	Per cent. of phosphor's soluble in acid $HgCl_2$.	Per cent. of total phosphorus soluble in acid $HgCl_2$.
Car. I	1.22	0.098	0.780	0.068	0.058	annealed	0.098	100.0
Car. I	1.22	0.098	0.780	0.068	0.058	719°	0.087.	89.8
Car. I	1.22	0.098	0.780	0.068	0.058	750°	0.051	52.0
Car. I	1.22	0.098	0.780	0.068	0.058	825°	0.018	18.3
Car. I	1.22	0.098	0.789	0.068	0.058	923°	0.015	15.3
Car. I	1.22	0.098	0.780	0.068	0.058	1023°	0.016	16.2

The evident influence of the amount of carbon present and the heat treatment upon the solubility of the phosphorus as given in the last column of the above table is best shown graphically in the diagram given below.



Full line = Carnegie Iron.
Broken line = N. S.
Dotted line = Cleveland.

The above work brings out the fact that phosphorus like carbon is capable of existing in steel in at least two forms and that

the influence of phosphorus upon the physical properties of steel in which it is contained is as much dependent upon the form of combination in which it exists as upon the quantity. This power of phosphorus to exist in two or more forms in steel with the varying influence on the brittleness of the steel according to the form present will, we think, account for many of the apparent inconsistencies in the statements usually made by metallurgists in regard to the behavior of this element. Much remains to be done upon the products of solution of iron and steel along the lines indicated either by the present paper or by that of Mackintosh,[1] or more recently by Juptner's paper, read before the British Iron and Steel Institute, May, 1897, before we shall be able to accumulate sufficient data to enable us to draw reliable conclusions as to the forms in which phosphorus may exist in iron and steel, the conditions under which the different forms are produced, and the influence of the different forms on the physical properties of the metals.

AN ELECTRICAL LABORATORY STOVE.

By M. D. Sohon.

Received July 7, 1897.

THIS apparatus has been designed to economically replace, as far as possible, the ordinary water-baths and gas burners used in the laboratory.

The stove is of copper, preferably cylindrical, about three

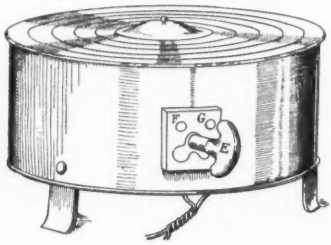


FIG. 1.

inches in height, exclusive of legs, and seven and a half inches in diameter. The top consists of the usual concentric rings; the bottom is open. The heating plate *A* is placed two inches

[1] *Trans. Amer. Inst. Min. Eng.*, 14, 385.

from the top, allowing ordinary flasks and casseroles to rest securely on the rings without touching the bottom. There is a clearance of one-fourth inch between the plate and sides of stove, allowing anything falling into the stove to pass through. The heating plate and body are independently fastened to the legs and may be quickly detached.

The heat is generated by the coils, *B*, of ordinary rheostat alloy, imbedded in silicate insulation, a half inch asbestos board, *C*, supports this and prevents the radiation of heat downward. A copper plate, *D*, turned over the edges, protects the coils and insulation from materials falling upon them, and strengthens the plate. Copper is preferable to the iron plate usually employed in rheostats, heating more rapidly and being less quickly attacked by reagents, and is easily replaced if destroyed.

The heating coil is in two parts of unequal size, either or both

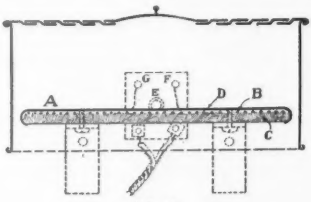


FIG. 2.

of which may be brought into use by means of the switch *E*, thus permitting of three variations of temperature without the use of other apparatus. The most convenient size of coils are such as to maintain the plate at about 90°C., 110°C., and 125°C.

Compared with the water-bath it is clean and dry and requires no attention. It is only necessary to *press the button* and it supplies immediately a constant and dry heat. The heat can be varied, and it is not affected by draught as are gas stoves, nor does it unnecessarily heat the laboratory. By the use of suitable coils or interposing resistance, the stove may be used with more volatile liquids. It especially recommends itself in connection with the distillation of inflammable liquids, extractions, etc., where danger from fire is to be avoided.

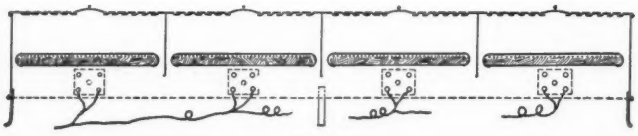


FIG. 3.

A group of the stoves, independently connected, is highly preferable to the large cumbersome water- or steam-baths generally employed.

THE ESTIMATION OF PHOSPHORUS IN STEEL.

BY R. W. MAHON.

Received August 12, 1897.

MANY analysts regard the titration of ammonium phosphomolybdate by standard alkali and acid with phenol phthalein as indicator as the best method for the routine determination of phosphorus in steel.

By two modifications of one of the approved processes for obtaining phosphorus in steel as ammonium phosphomolybdate, I have so shortened the operations as to enable one to execute the analysis in eight minutes, from receiving the drillings to obtaining the result. The results are accurate in the absence of arsenic. I have not experimented with the process in the presence of arsenic. No experiments have been made with steels containing silicon or carbon in considerable quantity. The process was devised for facile determination of phosphorus in steel containing scarcely any silicon, and low in carbon. It appears entirely probable that with high carbon and silicon, perfectly accurate results would be obtained. The two modifications I have to suggest are (1) effecting the partial neutralization in a different manner, and (2) precipitating at a higher temperature. Before the steel drillings are received, the following preparations for the analysis are made: Seventy cc. of water and thirty cc. of nitric acid (sp. gr. 1.4) are poured into a sixteen-ounce Erlenmeyer flask, a measured quantity of standard caustic potash solution and a little water are poured into a small beaker, the reading of the acid burette is recorded, and the filter is placed in its funnel, at the suction-pump, ready for use.

Four grams of drillings are placed in the flask containing the

acid, and this immediately placed over the gas. As soon as dissolved add three cc. of a standard solution of potassium permanganate, and boil until no longer pink. Add ten cc. of hydrochloric acid (sp. gr. 1.20), boil until clear, remove from gas, wait for a few seconds until the boiling has nearly ceased, and then add a mixture of fifty cc. of molybdate solution and ten cc. to fifteen cc. of ammonia (sp. gr. 0.90), made ready just before use. Pour into the middle of the flask, not down the side. Twirl the flask in both directions, successively, without delay. Shake the open flask for about one quarter of a minute. Filter and wash with cold water. Place the paper and precipitate in the beaker, containing an excess of caustic potash solution, add phenol phthalein, and determine the excess of caustic by the standard acid.

The two standard solutions are of the customary strength; the molybdate solution is made according to the following formula: 100 grams of molybdic acid are dissolved in a mixture of 200 cc. of ammonia (sp. gr. 0.90) and 200 cc. of water, and the solution filtered into 1,250 cc. of nitric acid (sp. gr. 1.20), blowing air through the mixture. Fifteen cc. of ammonia (sp. gr. 0.90) will neutralize fifty cc. of this solution, hence the amount of ammonia recommended in making up the mixture for use in an analysis. Ten to fifteen cc. of ammonia can be added, and if the mixture is kept cool during mixing no separation of molybdic acid will occur for some undetermined, but considerable time. This cold mixture can be satisfactorily used. It is, however, unnecessary to take the precaution of cooling during the mixing of molybdate solution and ammonia, if the mixture is used as directed. It is to be noted here that the graduated or other vessel used for mixing should invariably be rinsed before being used for a second quantity, as neglect of this sometimes causes separation of molybdic acid. The object of adding the mixture by pouring it into the middle of the solution and at once shaking the flask is to prevent separation of molybdic acid. This is the more elegant way of working, but is not indispensable, as the molybdic acid precipitated by very solid addition of the mixture, not poured accurately into the center, at once goes into solution again, when the prescribed course of manipulation is followed.

The temperature of the solution at the moment of addition of molybdate is about 105°C. The temperature of the mixture added is about 60°C. The amount of free acid before the molybdate is added is such that eighteen to twenty cc. of ammonia (sp. gr. 0.90) would, if added, produce a decided precipitate. A standard steel in which phosphorus had been determined many times with elaborate care by the molybdate-magnesia method, as 0.108, was used to make two series of estimations, titrating ammonia phosphomolybdate by standard caustic solution, one (A) with the older method of precipitating—that is adding ammonia in excess to the cooled solution of the steel, acidifying with nitric acid, and bring to 75° C. before adding molybdate solution; the other (B) with the method of precipitating described above—that is mixing molybdate solution and ammonia, in definite quantities, and precipitating a few seconds after removal from lamp.

Four estimations varying from 0.107 to 0.110. (A).	Twelve estimations varying from 0.108 to 0.111. (B).
0.108	0.108
0.107	0.111
0.110	0.109
0.107	0.111
——	0.109
Mean, 0.108	0.109
	0.110
	0.109
	0.110
	0.109
	0.109
	0.111
	——
	Mean, 0.110

In the series (B) above, the determinations were made to study the value of this method of precipitation, not to prove the time needed, a number of the estimations having been made simultaneously; consequently the filtration was only made immediately in some of the number.

In the following the time needed was the principal object of study, and each filtration was made a few seconds after adding molybdate:

Time consumed in analysis.	Phosphorus. Per cent.
Eleven minutes	0.108
Ten minutes	0.107
Eight and a half minutes	0.107

I have also carried out one, adding the potassium permanganate before the last few particles of steel had dissolved, and only boiling until the pink color nearly disappeared.

Time consumed in analysis.	Phosphorus. Per cent.
Seven minutes	0.109

Although successful here, this last procedure might fail with high carbon steel. All of the foregoing filtrates remained perfectly clear. The quantity of ammonia recommended is a vital point.

ESTIMATIONS BY METHOD B VARYING THE QUANTITY OF AMMONIA.

	Phosphorus. Per cent.
Five cc. of ammonia	0.096
Twenty cc. of ammonia	0.113

ESTIMATION BY METHOD B WITH VARIATION IN THE TEMPERATURE OF PRECIPITATION.

75° C., 0.110 per cent. phosphorus filtered in one minute.
65° C., 0.103 " " " " " " hour.
35° C., 0.108 " " " " " twenty-four hours.

This method of working is now in daily use, having been repeatedly checked by the older style, invariably with entire satisfaction. Used as a rapid method and with the details of manipulation described, the results are identical with those by (A). My principal use of it has been simply to lessen the number of operations needed; used in this way the drillings are placed in an empty flask, and the acid and water poured upon them; the filtration not necessarily being made after a fraction of one minute, nor with the suction-pump at all, but with the use of funnel and platinum cone, and filtering after the lapse of an indefinite time, varying from a few minutes to hours. Used thus, the results are 0.002 per cent. phosphorus higher.

The caustic solution is empirically standardized in these experiments by precipitates made in the older way (A); hence these appear as correct, and those by (B) as 0.002 per cent. phosphorus high. Were (B) precipitates used in standardization the record would make the results by (B) appear as correct, while those by (A) would average 0.106.

THE DETECTION OF FOREIGN FATS IN LARD AND BUTTER.

By C. B. Cochran.

Received August 12, 1897.

AS a means of detecting beef fat in lard I have made use of the following process: In a glass-stoppered twenty-five cc. graduated cylinder are introduced two cc. of the melted fat, and to this is added twenty-two cc. of fusel oil. The contents of the cylinder are warmed to about blood heat in order to obtain a perfect solution, and then allowed to cool slowly to a temperature of 16° to 17°C. This final temperature is maintained for two or three hours, during which time a crystalline deposit takes place, the amount and character of which varies with the fat under examination.

The deposit is then transferred to a filter paper and the fusel oil allowed to drain off as completely as possible. A part or the whole of the residue on the filter paper is then transferred to a test-tube and dissolved in ether. The mouth of the tube is closed with a plug of cotton and the crystals which form on standing are mounted in a drop of cottonseed oil and subjected to microscopic examination. By this method I have been able to detect the presence of a smaller amount of beef fat than I could detect when the sample was directly crystallized from ether.

A sample of lard containing ten per cent. of beef fat, when treated in this manner, will furnish a microscopic field showing abundant typical crystallizations of beef fat, which are usually much more numerous than lard crystals. When twenty per cent. of beef fat are present I have been unable to detect any lard crystals.

When the lard under examination contained five per cent. of oleostearin the crystals, although somewhat modified both in shape and manner of aggregating, yet gave decided evidence of the presence of beef fat.

A sample of lard containing two per cent. of oleostearin gave crystals so nearly like those formed from pure lard that I felt unable to say that the appearance either of the clusters or of the individual crystals indicated the adulteration.

Mutton tallow forms crystals very similar to those from beef.

So far as I know the one cannot be distinguished from the other by the character of the crystallization. All that has been said of beef fat in lard would apply also to mutton fat. The latter named fat behaves in lard like the former.

The amount of the deposit obtained from the fusel oil solution at 17°C. varies according to the character of the fat. A sample of beef suet, treated as indicated, gave a deposit of sixteen cc. The deposit obtained from a sample of oleostearin filled the tube to the level of the liquid. Pure lard in no case gave a deposit of over four cc. The relation between the amount of the deposit and the character of the fat is shown in the accompanying table and suggests a possible means of approximately estimating the percentage of beef tallow in lard, especially when taken in connection with the melting-point of the sample. Two or more pure lards of known melting-point, one high, the other low, could be kept as standards for comparison. The amount of deposit and melting-point of the sample of unknown origin compared with the deposit and melting-point of the standard would furnish a basis of comparison, as is done in the process devised by W. R. Stock. Before reading the amount of the deposit it is well to shake the cylinder, after which the deposit will settle evenly and more compactly.

The melting-points found in pure pig fats, given in the table, vary from 34°C. to 45°C., which is a little wider range than that given in the publications on lard by the United States Agricultural Department. The samples taken from different parts of the animal were all rendered in the laboratory and the melting-points determined by my assistant, Mr. C. S. Brinton. The method adopted by the Association of Official Agricultural Chemists was followed in detail in all cases.

In examining samples of butter or oleomargarine, add eight cc. of fusel oil to two cc. of the filtered fat; warm until a perfect solution is obtained, then cool to 16° or 17°C. A deposit will be formed which, in the few experiments I have made, has been greater in the case of oleomargarine than in butter. When this deposit is crystallized from ether very perfect crystals of large size are obtained. Up to the present time I have only examined six samples by this method, three of butter and three of oleomargarine, and as the crystals obtained in the two cases are, in some

No.	Sample.	Deposit at 17° C.	Melting-point.	Microscopic appearance.	Refractometer reading of sample.	Refractometer reading of soluble part.	Refractometer reading of insoluble part.
1	Pure lard	½ cc.	40.3° C.		46.0	46.1	40.0
2	90 per cent. lard, No. 1 10 " " oleostearin	4 cc.	43.2° C.	beef crystals abundant.			
3	80 " " lard, No. 1 20 " " oleostearin	10 cc.	44° C.	beef fat crystals. no lard crystals.			
4	70 " " lard, No. 1 30 " " oleostearin	18½ cc.	46° C.	beef fat crystals. no lard crystals.			
5	Oleostearin	24 cc. full	53.5° C.		39.1		
6	Beef suet	16 cc.	47° C.		40.8	42.0	39.2
7	Head fat of hog	less than 1 cc.					
8	90 per cent. head fat, No. 7 10 " " beef suet	1¾ cc.		beef crystals abundant. very few small lard crystals.			
9	80 " " head fat, No. 7 80 " " beef suet	2¾ cc.		beef crystals. no lard crystals.			
10	20 " " head fat, No. 7 10 " " oleostearin	3 cc.		splendid crystals.			
11	Mutton suet	18½ cc.	52.2° C.	resembling beef crystals.			
12	90 per cent. head fat, No. 7 10 " " mutton suet	1⅞ cc.		mutton crystals. very few lard crystals.			
13	80 " " head fat, No. 7 20 " " mutton suet	4 cc.		mutton crystals. no lard crystals.			
14	Pork side fat	1 cc.	34° C.		44.8	45.1	40.4
15	87½ per cent. side fat, No. 14 12½ " " beef suet	4½ cc.	39° C.		44.0	45.0	40.9
16	75 " " side fat, No. 14 25 " " beef suet	6 cc.	40.5° C.	beef fat crystals. a few lard crystals.	43.9	45.0	39.2
17	Pork kidney fat	less than 1 cc.	43.5° C.		44.5	45.3	40.2
18	90 per cent. pork kidney fat, No. 17 10 " " beef suet	1½ cc.			43.8		
19	Intestinal lard	4 cc.	45° C.	very long lard crystals.	42.5	40.0	40.0
20	Pure lard	1½ cc.	39° C.		45.0	45.8	41.1
21	Commercial lard	1½ cc.	40.3° C.	only lard crystals.			
22	" "	4½ cc.	41.5° C.	" " "			
23	" "	3 cc.	40.4° C.	" " "			
24	" "	5 cc.	38.8° C.	beef fat crystals.			
25	" "	3 cc.	36° C.				
26	" "	4 cc.	39° C.				
27	Pure lard	4 cc.	36° C.				

respects, similar, I do not feel able to make a positive statement in regard to the diagnostic value of this test in all cases. However, the difference in the appearance of the crystals, so far as I have yet observed, seems to be sufficiently great to serve as a means of distinguishing butter from oleomargarine.

From oleomargarine I have obtained perfect crystals of lard and of beef fat. Butter crystals are somewhat lard-like in appearance, but are much shorter and are frequently in rosette clusters.

The refractometer readings given in the table were made with a Zeiss butyrorefractometer. The first column gives the scale reading of the original sample, the second, or part soluble in the fusel oil at 17° C., and the third column, of the insoluble portion. The indices of refraction corresponding to the scale readings of this instrument can be found in Wiley's Agricultural Chemistry.

The fusel oil used in this work had a boiling-point of 129°C. and specific gravity of 0.8159.

CONTRIBUTIONS TO THE CHEMISTRY OF DIDYMIUM.

By L. M. Dennis and E. M. Chamot.

Received August 18, 1897.

THE announcement by Mosander[1] in 1842 of his discovery of a new element which he found accompanying cerium and lanthanum, and to which he gave the name didymium, was followed by careful and able investigations by Mosander and others upon the chemistry of this obscure group. The information which they obtained by means of purely chemical methods was, however, both meager and contradictory,[2] and it was not until the discovery by Gladstone[3] had put into chemists' hands a new analytical method that the results began to be fairly definite and satisfactory.

The spectroscope affords a means of detecting small amounts of earths yielding absorption spectra, and thus makes possible the preparation of purer compounds of such elements as cerium, lanthanum and yttrium, which give no absorption bands; but the most interesting results of the employment of spectroscopic

[1] *Ann. Chem. Pharm.*, 44, 125.

[2] Hermann: *J. prakt. Chem.*, 34, 182, doubts the existence of didymium.

[3] "On an Optical Test for Didymium," *J. Chem. Soc.*, 10, 219.

methods are seen in the gradual resolution of Mosander's didymium into a number of component earths. Gladstone[1] mentioned only two bands in the absorption spectrum of a didymium solution, while Erdmann[2] mapped seven lines, and said that there might be an eighth in the extreme violet. Rood[3] stated that there are twelve, and Bahr and Bunsen[4] gave measurements of eleven, while later observers[5] describe about twenty bands. These twenty bands which, ten years ago, Krüss and Nilson ascribed to didymium, show that the separation of old didymium into several elements had already begun, for they do not include several bands which had formerly been thought to be due to didymium, but which Boisbaudran[6] in 1878 had shown to be caused by a new element which he had separated and which he named samarium. In 1885 Auer von Welsbach[7] succeeded in separating didymium into two earths, which he called *neodym* and *praseodym*, but which, following the example of Krüss,[8] should be termed *neodidym* and *praseodidym*. These two earths have markedly different properties, the neodidymium giving rose red salts, while those of the praseodidymium are green. There can be little doubt, however, that both are composite and that neither one is an *element* in the present acceptation of that term. Krüss and Nilson,[9] upon examining didymium extracted from many different minerals, found that the same absorption bands varied in relative intensities in the samples of didymium from these various sources, and concluded that our present didymium probably consists of not less than nine elements. Crookes has made the suggestion that each element may yield but one absorption band, and says: "According to this hypothesis, therefore, neodymium and praseodymium must not be considered as actual chemical elements, but only the names given to two groups of molecules into which the complex molecule didym-

1 *Loc. cit.*

2 *J. prakt. Chem.*, **85**, 394.

3 *Chem. News*, **6**, 140.

4 *Ztschr. anal. Chem.*, **5**, 109.

5 Lecoq de Boisbaudran: Spectres lumineux, Texte, p. 87; Krüss and Nilson: *Ber. d. chem. Ges.*, **20**, 2146.

6 *Compt. rend.*, **89**, 212.

7 *Monatshefte*, **6**, 477.

8 *Ann. Chem.* (Liebig), **265**, 3. Krüss and Nilson ask (*Ber. d. chem. Ges.*, **20**, 2166), "Was bedeutet 'dym'?"

9 *Ber. d. chem. Ges.*, **20**, 2166.

ium splits up by one particular method of fractionation."[1] Thompson[2] thinks that the six bands in the blue and violet, having approximately the wave-lengths 482, 476, 469, 462, 444 and 428, are due to at least five different components. Becquerel and others similarly state their belief in the compound nature of didymium.

It would seem natural, then, that having become convinced of the compound character of old didymium, chemists should at once undertake the isolation of the various constituents of this earth. Many of our ablest investigators have endeavored to do this, but the various bases are so closely allied in their chemical characteristics that, up to the present time, only approximate separations have been effected, and these separations have, for the most part, been accomplished by the employment of methods of fractionation that constant use has shown to be capable of giving only imperfect separations, and that at the expenditure of much time and labor. The need, then, at the present time is for new methods of separation or critical examination of the older methods, so that we may be able to obtain sharper results in shorter time. The experimental work described below was undertaken with this end in view, and while we are as yet unable to offer new data concerning the components of didymium, we trust that our observations upon the splitting of didymium may be of interest to workers in this field.

The mixture of earths, which was used for the work, was extracted from monazite sand from Brazil. The sand was decomposed by sulphuric acid and the rare earths were separated from the other elements present by the usual methods. The large amount of cerium which accompanied the other earths was removed by the chlorine method devised by Mosander, as this was found to be more suitable to the treatment of large amounts (we had in hand 9,200 grams of the dry oxalates) than was the fusion of the nitrates with a mixture of sodium and potassium nitrates.[3]

The following procedure was finally adopted: Tall bottles of a capacity of from fifteen to twenty liters, were fitted with two-hole rubber stoppers, one hole carrying a glass tube of about

[1] *Chem. News*, 54, 27.
[2] *Chem. News*, 55, 227.
[3] Dennis and Magee: This Journal, 16, 649.

one cm. diameter, reaching to the bottom of the bottle, the other an exit tube ending just below the stopper. The bottles were then connected in series by rubber tubing, so that the chlorine would pass through all of them in turn. Eight to ten liters of the moderately dilute solution of nitrates of the earths was poured into each bottle and a strong solution of potassium hydroxide was then added until the reaction was distinctly alkaline. Each bottle was filled with water to within six inches of the top. Chlorine gas was then led into the first bottle at a rapid rate, any unabsorbed gas passing into the second. By shaking the first bottle from time to time, it was found easy to determine when no further absorption of gas was there taking place. The treatment was then continued a little longer, when the first bottle was removed and the gas passed directly into bottle number two, a fresh bottle being placed at the end of the row. By operating in this way there were always three bottles in line, the last being a fresh one. No loss of chlorine could occur and the operation being continuous, a large amount of material could be treated in a short space of time. After allowing the chlorinated portions to stand until the insoluble ceric hydroxide had settled, the supernatant solution was siphoned off and filtered. The clear solution thus obtained contained the earths of the didymium and yttrium groups free from ceria. This solution was transferred to tall glass cylinders of about twenty liters capacity and the liquid was violently mixed by means of the air blast or a Rabe turbine, oxalic acid, meanwhile, being slowly run in until in excess. The precipitate was allowed to settle, the supernatant liquid was drawn off with a siphon and the cylinder was again filled with distilled water. After each addition of water the contents of the cylinder was stirred for an hour, and the above operation was repeated until the wash-water was free from chlorides. More didymium was separated from the insoluble ceric hydroxide by repeatedly washing the latter with water and then dissolving it in hydrochloric acid, adding potassium hydroxide and chlorinating once more. The chlorine which was used came from a cylinder containing ninety pounds of the liquefied gas. This was found to be cheaper and easier to control than the production of the gas by the usual methods.

The thoroughly washed oxalates of the earths freed from

cerium as above, were dried in an air-bath, ignited in large platinum dishes and dissolved in dilute nitric acid. The clear pink solution showed no trace of cerium when tested with hydrogen peroxide and ammonium hydroxide, and was therefore ready for fractionation, unless it was desired to first remove the earths belonging to the yttrium group. To remove the yttrium group, the solution of the nitrates of the earths was diluted and placed in a tall cylinder whose contents could be rapidly stirred from top to bottom by means of a turbine. Potassium sulphate was added in sufficient quantity to constantly maintain quite a thick layer of the crystals on the bottom. In this way a very satisfactory separation can be accomplished in a far shorter time than by any method with which we are familiar. In the absence of a turbine, almost as good results can be obtained by using a strong air blast, but in this case a quantity of potassium sulphate should be maintained near the surface of the liquid by means of a percolator or similar device.

The precipitate from the above treatment contained the double sulphates of the didymium group. It was washed repeatedly with a saturated solution of potassium sulphate and was finally thrown upon a Witt plate and sucked dry with the suction-pump. The insoluble sulphates were then dissolved in a moderately dilute ammonium acetate solution,[1] filtered, and the clear liquid precipitated with ammonium hydroxide, hydrochloric acid sufficient to decompose the ammonium acetate having first been added. The hydroxides were washed as usual until no further test for sulphate could be obtained by barium chloride. These hydroxides were then dissolved in nitric acid and this solution was used in the subsequent work. In one case in which the yttrium group was removed after a series of fractional crystallizations had been completed, it was found that the double potassium sulphate salts of the earths at the neodidymium end of the series dissolved much more easily in ammonium acetate than did the praseodidymium fractions.

The method of fractionation which was first tried was that of Welsbach,[2] but the details which he gives, especially concerning the strength of acid and the amount of water to be added, are

[1] Urbain: *Bull. Soc. Chim.*, 15, 349, *1896*.
[2] *Monatshefte*, 6, 477.

vague and our results when following his directions as closely as possible, were quite unsatisfactory.

It was soon found that the results of the fractionation were greatly influenced by the amount of the nitric acid present. If a large amount of nitric acid is added, the lanthanum double salt separates in the first two or three fractions, and the subsequent splitting of the didymium is then very slow; if, on the other hand, the acid be too weak, a long series of fractions which show but slight differences, is obtained.

The method used by Bettendorff[1] with material high in lanthanum and low in didymium was next tried, but as our oxides contained didymium in excess, the results were again unsatisfactory. It was found, however, that although Bettendorff's method did not produce much effect on the didymium, it appeared to rapidly remove samarium, the absorption bands of this earth being quickly eliminated, whereas the didymium bands showed but little change.

While working upon Bettendorff's scheme of separation, a series of fractions prepared by Welsbach's method had been allowed to stand undisturbed for several days. Upon examining the middle members of this series it was noticed that where the solution had crawled up on the sides of the dishes and crystallized, the crust thus formed was of a deep rose-red color, while the crystals which had formed in the solution were of an entirely different shade of pink. The two kinds of crystals were carefully separated and dissolved in water. The absorption spectra of the two solutions showed that a marked splitting of didymium had taken place, the crystalline crusts which had formed on the sides of the dishes giving a spectrum in which the neodidymium bands were much stronger than those assigned to praseodidymium; there was also a remarkable increase in the intensity of the samarium bands. An aqueous solution of some of the other crystals showed a corresponding increase in the intensity of the praseodidymium bands.

These observations naturally led to the idea that the splitting of didymium might be more rapidly attained by abandoning the customary procedure of concentration by heat and rapid crystallization, and subjecting the solutions to spontaneous evaporation

[1] *Ann. Chem.* (Liebig), **256**, 163.

and slow crystallization. The results exceeded our expectation, for upon making a series of fractions in this manner, very marked spectrum changes were speedily obtained. The sharpness of the separation by slow crystallization is illustrated by the two absorption spectra shown in Plate II. Only the lines in the blue and violet are here mapped, since the changes are greatest in that portion of the field. A portion of the solution containing the double ammonium nitrate was allowed to stand for five days and slowly crystallize. The mother-liquor was then poured off. Its spectrum (II, *a*) shows very strong neodidymium bands, and praseodidymium bands which are relatively much weaker. A saturated solution of the crystals gave the spectrum shown in II, *b*, in which the neodidymium bands are much weaker than those of praseodidymium. The thickness of the solution in each case was ten mm. To test more thoroughly the efficiency of this slow crystallization, somewhat over one kilo of oxides of monazite earths, free from ceria, was converted into double ammonium nitrates, a small amount of nitric acid added, and the whole evaporated to such a concentration that partial crystallization took place only after forty-eight hours. The mother-liquor was then poured off and set aside to crystallize spontaneously. The crystals were dissolved in dilute nitric acid by the aid of heat, and allowed to stand. The crystals and mother-liquor thus obtained were treated as before. After about twenty such fractions had been formed, all those of about the same color, shade, and intensity were united and each portion thus formed was then fractioned separately, similar fractions being from time to time united so as to form a long unbroken series. This process was continued until a series of 105 fractions of the double nitrates had been obtained.

It was found that while the greater part of the lanthanum separated in the first few portions, much of it, contrary to expectation, was carried along to the latter fractions, depositing gradually with the other earths until apparently a certain relative concentration of the different earths was reached, when white crystals again separated, the subsequent fractions becoming more and more intensely pink, until finally the beautiful rose-red salts of the neodidymium and samarium earths were formed. Then suddenly light-colored crystals would appear in the suc-

ceeding fractions, and there would again be seen the same series of color changes as had before been observed. For example, fractions 1 to 10 were almost pure lanthanum ammonium nitrate, 11 to 16 showed a growing intensity of the characteristic green tint of the praseodidymium components, 17 was whitish with a tinge of brownish pink, which increased in intensity to 24, 25 had the same tint as 17, but the succeeding fractions up to 29 were decidedly pink, the color growing rapidly darker; 30 showed another falling off to a light color, as did 38, 48, 57, 72, 78, 80, and 88. Above 88 the pink color increased to the end of the series. Throughout the whole series, the spectra of the light-colored crystals, no matter in what portion of the series these lighter crystals had appeared, showed the bands of praseodidymium much more strongly than those of the neodidymium earths, and the samarium bands were generally almost invisible.

Determinations, by the method of Gibbs, of the atomic mass of the earths in the almost colorless fractions gave on the average $\dddot{R}$ = about 139. Assuming then that these light-colored fractions consisted largely of lanthanum, an examination of the series disclosed the fact that the most marked splitting of didymium was noticeable in fractions but little removed from the light-colored portions, and that the amount of free nitric acid present exerted a powerful influence upon the character of the crystals. It seemed apparent, also, that slow crystallization had been much more effective than the rapid process hitherto employed.

Further experimentation led to the adoption of the following method, which has yielded, on the material from Brazilian monazite, most excellent results:

To a moderately concentrated solution of nitrates of the rare earths, free from ceria and high in lanthana, ammonium nitrate is added in the proportion of four molecules of NH_4NO_3 to one of R_2O_3 where $\dddot{R}$ can be assumed to have a mean atomic mass of 142. Sufficient nitric acid (sp. gr. 1.42) is then added to the solution so as to have one part of acid to four parts of water, by volume. The solution, after thorough stirring, is then evaporated to such a point that nearly all the salts will crystallize out in from twenty-four to thirty-six hours. The small amount of

Plate I.

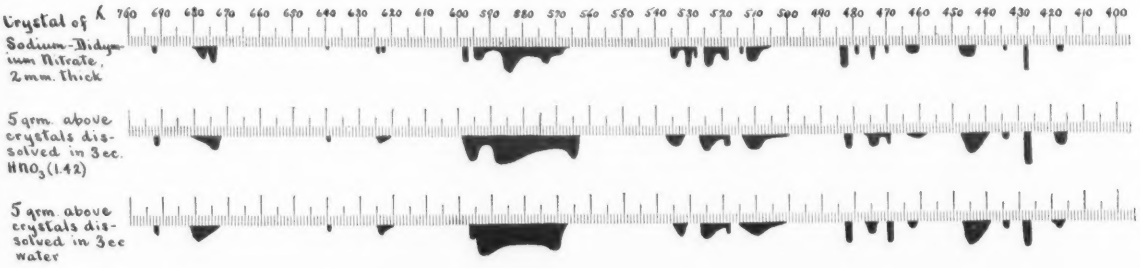

Crystal of Sodium-Didymium Nitrate. 2 mm. thick
Å 740 690 680 670 660 650 640 630 620 610 600 590 580 570 560 550 540 530 520 510 500 490 480 470 460 450 440 430 420 410 400
5 grm. above crystals dissolved in 3 cc. HNO_3 (1.42)
5 grm. above crystals dissolved in 3 cc water

Plate II

Showing sharpness of separation by slow crystallization.

Plate III

mother-liquor is then set aside and allowed to stand undisturbed until a good crop of crystals has formed; the mother-liquor from this fraction is poured off and allowed to crystallize spontaneously as before. The large crop of crystals from the original solution is dissolved with the aid of gentle heat, in such an amount of moderately dilute nitric acid (1:4) that crystals begin to form in from five to ten hours. After a large proportion of the salts of the earths has separated, the mother-liquor is poured off and allowed to crystallize spontaneously. The crystals are dissolved as before in 1 : 4 nitric acid. The same treatment is given to all crystals and mother-liquors obtained. From time to time such crystals and mother-liquors, irrespective of their position in the series, whose absorption spectra are approximately similar and whose colors are alike, are united and serve as the starting-point of new series of fractions, which in turn are similarly united. The absorption spectra of the different fractions should be constantly compared and like fractions united, since the rapidity of the method will depend very largely upon the judgment of the operator in properly uniting the various members of the series. The absorption spectra of the different fractions can easily be observed by reflected light, as they lie in the dishes, it being simply necessary to direct a pocket spectroscope toward them. It should be remembered, however, in comparing these spectra, that the spectrum of a crystal is generally very different from that of its solution.[1]

It is seldom, if ever, necessary to remove the crystals from the dishes in order to sufficiently free them from the mother-liquor; they form compact masses, and the supernatant solution can be thoroughly removed by simply tipping the evaporating dishes and leaving them in that position for a short time.

As the neodidymium end of the series is approached, lanthanum ammonium nitrate which has been obtained in the first fractions, is added to the fractions, together with a little nitric acid (1 : 4), and the whole is gently heated, thoroughly stirred, and set aside to slowly crystallize. The amount of lanthanum

[1] Several years ago Lawrence Smith and Lecoq de Boisbaudran (*Compt. rend.*, 88, 1167) called attention to the change which is caused in the absorption spectrum of didymium when nitric acid is added to the aqueous solution. Becquerel has described (*Compt. rend.*, 104, 165) the variations in the spectra of the crystalline compounds of didymium. In further illustration of these peculiar phenomena, we have ventured to present the three spectra as shown in Plate I.

salts to be added will, of course, depend upon the volume of the solution and the proportion of didymium earths present.

The above method possesses one serious drawback. The double ammonium nitrates of the didymium earths are extremely deliquescent, and in a moist atmosphere their solutions refuse to crystallize. By carrying on the work during the winter months in dry, steam-heated rooms, however, no difficulty whatever was experienced.

When the work was conducted in a fairly dry atmosphere it was found that more satisfactory results could be obtained by adhering to the use of ammonium nitrate than by changing, for the last series of fractions, to sodium nitrate, as Welsbach suggests. For example, it was found possible to obtain in one month, from 800 grams of the mixed oxides, a sample of praseodidymium, which in a saturated solution ten cm. thick, showed only the faintest traces of the bands ascribed to neodidymium.

The fact that the presence of lanthanum facilitates the separation of these two components of didymium was mentioned by both Welsbach and Bettendorff. Schottländer appears to be the only one who added the lanthanum salt to some of his later fractions, but he seems to have discontinued this addition after a few series of fractions had been prepared.[1]

In our work it was found that whenever lanthanum had been largely removed from the solutions under treatment, crystallization took place only with great difficulty and such solutions, when they did crystallize, gave fractions that differed but little from one another in their absorption spectra. If, however, all of these same fractions were again united and a small amount of lanthanum ammonium nitrate added, an immediate change took place in the absorption bands of the different fractions then obtained. Earths high in praseodidymium separated in the early fractions while the last fractions gave only faint bands of this component. The greater part of the samarium seemed to remain in the last mother-liquor. The results of one such crystallization after the addition of the lanthanum salts are shown in Plate III, *a*, *b*, *c*. *a* shows the spectrum of the fraction before the addition of lanthanum. One hundred and twenty grams of lanthanum ammonium nitrate was then added

[1] *Ber. d. chem. Ges.*, **25**, 392.

and the solution allowed to slowly crystallize. *b* gives the spectrum of the mother-liquor from the resulting crystals, showing increase in intensity of the neodidymium and samarium bands; *c* is the spectrum of the solution of the crystals, showing marked weakening of the neodidymium bands, and strengthening of the praseodidymium.

These changes in the absorption bands cannot be due merely to the presence of lanthanum in the solutions, since the effect of such addition was repeatedly tried on different solutions and no changes in the character of the absorption bands could be detected other than a uniform weakening due to dilution. As soon, however, as crystallization began, the crystals and mother-liquor showed differences from the original solution.

In fractioning by this method, it was noticed that the heavy band in the orange was not resolved into the component bands described by Welsbach, even when the remainder of the lines had undergone marked changes, this observation confirming the statement of Crookes that "probably didymium will be found to split up in more than one direction, according to the method adopted."[1] In certain fractions the relative intensities of the bands bore out the observations of previous investigators as to the compound nature of both neodidymium and praseodidymium. Thus in one portion the neodidymium band λ-428 was intense, while the other didymium bands were comparatively faint. We also obtained fractions which showed the band λ-443 much more strongly than any other bands.[2]

CORNELL UNIVERSITY, August, 1897.

THE TITRATION OF STANNOUS SALTS WITH IODINE.

BY S. W. YOUNG.

Received July 31, 1897.

FRESENIUS[3] describes very briefly a method by Lenssen, for titrating stannous chloride with iodine in neutral or faintly alkaline solution. As was pointed out in a previous paper,[4] it was evident that the action of iodine on stannous chloride was a quantitative one also in acid solution. Further study has con-

[1] *Chem. News*, 54, 27.
[2] See also Crookes: *J. Chem. Soc.*, 56, 260.
[3] Syst. Quant. Chem. Anal., 1st Am. Ed., p. 342.
[4] This Journal, 19, 517.

firmed this point, and it has been found perfectly possible to titrate stannous salts with great accuracy in acid solution, provided, of course, there are neither oxidizing or reducing substances also in the solution.

The method of operation is very simple, and consists simply in bringing the stannous salt into solution, preferably with dilute hydrochloric acid, adding starch paste and then standard iodine solution until a blue color is produced. The essential precautions are:

(1) Care to prevent oxidation of the stannous salt solution by undue exposure to air. The solution should be prepared rapidly and titrated immediately.

(2) Since the titration is carried on in acid solution, it is essential that the potassium iodide used in the preparation of the standard iodine solution should be particularly free from iodate, since if this latter were present, it would be decomposed rapidly by the acid in the solution titrated and considerable iodine would be set free from the action of the iodic acid on the potassium iodide. This would, of course, make the results of the titration too low.

As thiosulphate cannot be satisfactorily used in acid solution to titrate against iodine, it will be found very convenient to use a dilute solution of stannous chloride for that purpose. This solution may most conveniently be kept under coal oil, and since its strength changes rapidly even then, its relationship to the iodine solution should be very frequently determined—at least once a day.

The most convenient method for preparing the stannous chloride solution is to treat metallic tin with concentrated hydrochloric acid until the action becomes rather slow. Then filter rapidly through cotton wool, preserving this solution under oil for future use. To prepare from this the dilute solution for titration, the standard of the strong solution is roughly determined, and a portion is then diluted to the desired strength and the standard of this is accurately determined.

In this work the iodine has been first standardized by the usual method with thiosulphate.

Following are the results of determinations made with the method, of the percentage of stannous chloride in the salt

$K_2SnCl_4.2H_2O$, described by Richardson.[1] The agreement of the results is very good. Compared with the theoretical the values run a trifle high (three-tenths to four-tenths per cent.).

The cause of this, it was thought, might lie in the fact that the standardizing of the iodine solution took place under entirely different conditions from those existing in the actual determination, *i. e.*, in neutral instead of acid solution.

In general the standard of iodine by thiosulphate is likely to be a trifle high.

The following method for standardizing was then tried: A fresh solution of stannous chloride was prepared of such strength as to be approximately equivalent to the iodine solution. Portions of C. P. potassium bichromate were weighed out (about two-tenths gram). These were titrated with the stannous chloride solution until the bichromate had been completely reduced and then titrated back with iodine solution until the starch iodine blue was produced. The green color of the chromium chloride does not interfere.

The reaction between potassium bichromate and stannous chloride being

$$K_2Cr_2O_7 + 3SnCl_2 + 14HCl = 2KCl + 2CrCl_3 + 7H_2O + SnCl_4,$$

and the relationship between the iodine and the stannous chloride solutions being accurately determined, the stannous chloride equivalent of the iodine solution may be calculated. By this method the stannous chloride equivalent was found to be 0.004150 gram per cubic centimeter.

By the thiosulphate method the standard of the same solution had previously been found to be 0.004178 gram per cubic centimeter.

Following are the results of the titration by the thiosulphate standard upon the salt $K_2SnCl_4.2H_2O$.

50.95	50.85	51.05
51.17	50.70	50.88
50.87	50.88	.....

Following are the same results calculated by the bichromate standard:

50.60	50.51	50.72
50.82	50.36	50.53
50.52	50.53	.....

[1] *Am. Chem. J.*, 14, 91.

The results are in percentages of stannous chloride. The theoretical percentage is 50.49.

The method has the advantage of being less interfered with by the presence of other substances, than is the usual method of titrating with ferric chloride and permanganate. The titrations may be made in the presence of iodides and bromides and in the presence of iron salts, these cases conflicting with the permanganate method.

Although definite data have not yet been obtained, it is believed that the method may be applied in the presence of many organic bodies also.

STANFORD UNIVERSITY,
July 15, 1897.

THE VOLUMETRIC DETERMINATION OF THE NITRO GROUP IN ORGANIC COMPOUNDS.

BY S. W. YOUNG AND R. E. SWAIN.

Received July 31, 1897.

AS was pointed out in the previous paper, "The Titration of Stannous Salts with Iodine," it is possible to accurately determine the amount of stannous tin in a solution by means of standard iodine. This suggested the possibility of determining certain oxidizing agents by utilizing the reducing power of stannous chloride. The following results show that the process is applicable to the determination of the nitro group, at least in dinitrobenzene.

There are requisite for the method :

(1) A standard solution of iodine whose value is accurately known.

(2) A dilute solution of stannous chloride, preferably of such strength that one cc. of it is equivalent to about three cc. of the iodine. The object of using so strong a solution is to avoid the necessity of using too large a volume of it.

The process of determination was as follows :

Weighed samples of pure dinitrobenzene, which had been recrystallized from alcohol, were placed in Erlenmeyer flasks, holding about 500 cc. Ten to fifteen cc. of alcohol were added in order to bring the samples into solution. The relationship between the iodine and stannous chloride solutions was now accurately determined. The flasks were then all connected, in

series, with a Kipp generator for carbon dioxide, and when filled with the gas, the stopper of each was removed, and so much of the stannous chloride solution added as was estimated to be sufficient to reduce the dinitrobenzene and leave a small excess (ten to twenty cc. excess is sufficient). Connection with the gas generator was again established, and a slow stream of the gas was kept passing through the apparatus throughout the process of reduction. The flasks are heated on the water-bath to hasten the process. Under these conditions one and one-half to two hours was found sufficient time to complete the reduction. The addition of twenty to twenty-five cc. of strong hydrochloric acid appeared to hasten the process somewhat.

Upon completion of reduction the flasks are removed and the excess of stannous chloride titrated with standard iodine solution, and the net volume of stannous chloride calculated.

The most likely reaction between the nitro group and stannous chloride is as follows:

$$RNO_2 + 3SnCl_2 + 7HCl = RNH_2.HCl + 3SnCl_4 + 2H_2O.$$

The results obtained confirm this.

The reaction between iodine and stannous chloride being

$$2SnCl_2 + 4I = SnCl_4 + SnI_4,$$

it follows that a factor can be found which will be the nitro equivalent of the iodine solution. Then knowing the relationship between the iodine and stannous chloride, we can calculate the volume of iodine equivalent to the volume of stannous chloride used, then from the nitro equivalent of the iodine we can easily calculate the percentage of nitro group in the body. The nitro factor of the stannous chloride might, of course, be determined, but would not be so satisfactory as that of the iodine, on account of the rapidity with which the stannous chloride changes.

Following are eight selected results of the determinations upon dinitrobenzene:

54.68	54.83
54.51	54.64
54.76	54.66
54.94	54.92

The theoretical percentage is 54.76.

Following are eight results obtained from *one series* of deter-

minations, no results being omitted. These show the reliability of the method:

54.63	54.44
54.48	54.49
54.61	54.44
54.40	54.44

With careful work the method presents no particular difficulty.

Of course it does not follow from the foregoing that the method is very generally applicable to nitro bodies. Investigations will be made to determine the limits of its utility.

STANFORD UNIVERSITY,
July 20, 1897.

A MODIFIED METHOD OF FINE SILVER ASSAY.

BY AUGUSTUS E. KNORR.

Received August 23, 1897.

IN the government assay offices and in the laboratories of silver refineries the assay of fine silver is usually performed according to the method of Gay-Lussac. Two solutions are required, a standard solution of sodium chloride, 100 cc. of which will very nearly precipitate one gram of pure silver, and a second solution, the exact decimal of the former, by means of which the titration is carried to an end. The quantity of fine silver weighed for assay is so adjusted that it will contain one or two milligrams over one gram of pure silver, a preliminary fine assay being made, if necessary, in order to determine the exact quantity to be taken. It is dissolved in nitric acid, 100 cc. of the standard solution of salt are added, and by vigorous shaking the precipitate is caused to collect. In the clear solution the excess of silver is precipitated by means of the decimal solution, added one cc. at a time, and shaken before each addition, in order to observe the cloudiness produced. Fractions of one cc. are estimated by the depth of cloudiness on the last addition of decimal solution causing a perceptible precipitation.

This tentative method, though accurate, is apt to be tedious, much time being consumed if the fineness of the silver is not known within 0.002 to 0.003. About three minutes shaking is required in order to obtain a perfectly clear solution, which is very irksome if there is no mechanical agitator at the operator's disposal.

I have for some time used a modification of this method, largely obviating the shaking, and have found it both speedy and accurate. Instead of making the final titration with the decimal solution of sodium chloride, I prefer to titrate out with potassium thiocyanate according to the method of Volhard, using a ferric salt as an indicator. The standard solution employed is the same as in the original method, variations due to temperature and evaporation being eliminated by running a proof of pure silver with each daily set of assays. The solution of potassium thiocyanate is not an exact decimal of the first, but is standardized against pure silver so that one cc. will precipitate exactly one milligram of silver. A correction for this solution is not required, since in this dilution possible variations would fall beyond the limit of accuracy, which I place at 0.2 to 0.3 milligram. Results are stated in milligrams of silver per thousand.

In performing the assay exactly one gram of the sample is weighed into a well annealed bottle (eight ounce), fitted with an accurately ground stopper; nitric acid, diluted with about two volumes of water free from chlorine, is added, and solution hastened by placing on a hot iron plate. Heating should be continued until the last traces of nitrous acid have been expelled, which would otherwise interfere with the accuracy of the method. Two proofs of pure silver are weighed and dissolved in the same manner; it is not necessary to weigh an exact gram, but the actual weight taken should be accurately ascertained.

When the nitrous fumes have disappeared, enough water is added to prevent crystallizing of the silver nitrate, and 100 cc. of standard salt solution, delivered with great accuracy from an automatic pipette, is run into each assay. The stopper is inserted and the solution shaken until the silver has collected, when it is filtered, five cc. of a solution of ferric ammonic alum added, and the thiocyanate solution run in from a burette until the characteristic color of ferric thiocyanate no longer disappears. This titration should be performed in the cold.

Suppose, for instance, that 1001.3 milligrams of pure silver had been taken for a proof and eight and four-tenths cc. of thio-

cyanate (equal to eight and four-tenths milligrams silver) had been required, then the titer of the salt solution is

$$1001.3—8.4 = 992.9.$$

The standard of the salt solution having thus been obtained from the average of two proofs, the fineness of the assays is found by adding the number of cubic centimeters of thiocyanate solution required to the standard found.

Copper and other impurities liable to be found in fine silver do not interfere with the accuracy of this method. It is necessary to separate the silver chloride by filtration because it slowly decomposes silver thiocyanate, and the wash-water must be free from chlorine.

I have repeatedly tested this method and found it accurate, as shown by the following data taken at random from my note book :

	Milligrams taken.	Thiocyanate. cc.	Standard.	Thiocyanate. cc.	Milligrams found.	Difference.
Proof	1000.0	— 8.5	= 991.5			
	1000.0	— 8.5	= 991.5			
			Average, 991.5			
Fine silver taken.	996.7		991.5	+ 5.3	= 996.8	+ 0.1
	996.9		991.5	+ 5.2	= 996.7	— 0.2
	998.9		991.5	+ 7.5	= 999.0	+ 0.1
Proof	1000.0	— 7.0	= 993.0			
	1000.4	— 7.5	= 992.9			
			Average, 993.0			
Fine silver taken.	994.0		993.0	+ 1.0	= 994.0	..
	997.0		993.0	+ 4.2	= 997.2	+ 0.2
	999.0		993.0	+ 6.3	= 999.3	+ 0.3
Proof	1000.0	— 8.2	= 991.8			
	1000.0	— 8.0	= 992.0			
			Average, 991.9			
Fine silver taken.	998.0		991.9	+ 5.9	= 997.8	— 0.2
	1001.8		991.9	+ 9.8	= 1001.7	— 0.1

SOME NEW FORMS OF APPARATUS.

By Augustus E. Knorr.

Received August 23, 1897.

I. AN AUTOMATIC FILTERING SIPHON.

In order to avoid the constant attention required in filtering large bulks of liquids, the following device has been found useful and an improvement on Mariotte's bottle. In using the latter any sediment or precipitate will go into the filter first and greatly retard the operation. The siphon consists of a glass tube bent after the usual fashion, as shown in Fig 1, *a*, and it is adjustable by means of a wire support laid over the top of the beaker or vessel containing the solution to be filtered. The longer limb is slightly expanded at the end and a conical valve ground in; the valve has a ball blown on and a knob at the opposite end of the stem, which prevents it from falling out of the tube having a constriction to engage the knob (shown in Fig. 1, *b*). The glass bulb causes the valve to float on the liquid in the funnel, rising as it fills until the valve is pressed home, when the supply of liquid is interrupted, only to admit a fresh quantity when the level again falls. The wire support and manner of placing it on the beaker is shown in Fig. 1, *c*. It is made of two pieces of stout wire twisted about a piece of brass tubing one inch long and fastened with a drop of solder. A short piece of rubber tubing slipped over this allows the shorter limb of the siphon to be adjusted by sliding up or down. Large bulks of solutions can be filtered through small filters, which is often desirable when there is only a small precipitate, and the latter is left undisturbed until nearly the entire solution has been filtered. A suction-pump can be employed at the same time if desired.

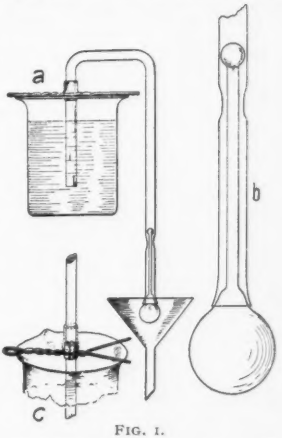


Fig. 1.

This device can be equally well employed in evaporating large quantities of water, and dishes down to the smallest size can be used, which is often an advantage, for instance, in water analysis; when once put in operation it can be left over night with perfect safety.

The operation, filtration, or evaporation having been completed, the siphon is washed out by removing the tip from a wash-bottle and blowing a stream of water through the shorter limb.

2. A NEW FORM OF GAS GENERATOR.

The gas generator here described has been found a source of great comfort in metallurgical work, where as in the analysis of refined copper it is not an infrequent occurrence to precipitate fifty to 100 grams of metal at a time in the form of sulphide. Fig. 2 represents the apparatus in its simplest form. The iron sulphide is contained in a calcium chloride jar and is decomposed by allowing hydrochloric acid, diluted with its own bulk of water, to trickle over it drop by drop. The spent acid collects at the bottom, and reaching the level of the U-shaped siphon, it will run out as fast as supplied. It may be discharged directly into the sewer, or a large bottle may be placed under the overflow, to be emptied from time to time. The siphon tube is the novel and essential feature of the apparatus, allowing no spent acid to foul the iron sulphide, while at the same time forming a perfect hydraulic seal against any escape of gas. It must be made sufficiently long for the column of liquor contained in it to overcome the pressure of the liquor in any precipitating vessel of ordinary size. For the same reason the stem of the acid bulb must be at least six or eight inches long.

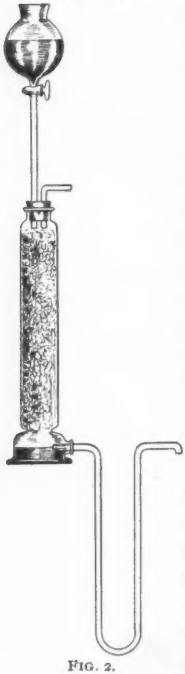


FIG. 2.

Fig. 3 shows a larger and somewhat more elaborate form of this generator made for the special purpose of supply-

ing very large quantities of hydrogen sulphide, where the smaller apparatus would require refilling every day or two. A large druggist's percolator of heavy glass, holding twenty or thirty pounds of iron sulphide was fitted into a calcium chloride jar, acting as a support and at the same time forming one limb of the siphon. The other limb was made of glass tubing appropriately bent. In order to avoid an inconvenient length of the stem of the acid bulb, the top of the latter was made to communicate with the interior of the generator through a T in the delivery tube and proper rubber connections. This equalizes the pressure above and below the acid and allows it to fall by its own gravity. In an apparatus of this size the flow of acid does not immediately answer changes in the speed of acid supply. In order to regulate it, it was found convenient to observe the flow of acid through a small bulb blown on just below the stop-cock and containing a projecting nipple, because after a short time the glass of the generator becomes covered with a black coating through which it is impossible to observe the drops of acid. The top of the percolator was closed with a six-inch rubber stopper permanently sealed in, while the stem of the acid bulb passed through a second rubber stopper, one inch in diameter, fitted into the first. In filling the apparatus only the small stopper is removed, and it was found advisable to use only coarse pieces of sulphide, powder and finer particles having a tendency to wash down and choke the throat of the percolator in a short time. A large acid reservoir placed on a shelf above the acid bulb is a convenience but not a necessity. The whole apparatus was securely clamped against the outside of the hood,

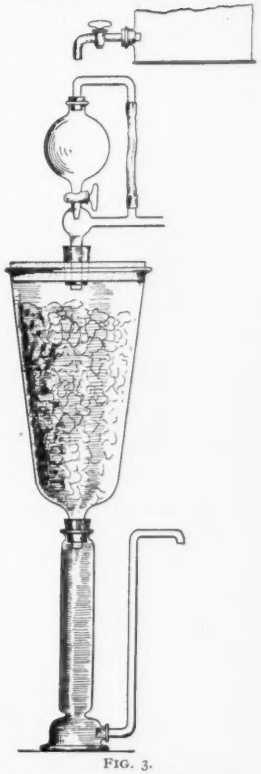


FIG. 3.

only the delivery tube projecting into the same. This generator in daily and almost constant use has been found to work without refilling or other attention for three months at a time, and would perhaps be best appreciated in college laboratories and others requiring an abundant and reliable supply of hydrogen sulphide. It can also be advantageously employed for generating carbon dioxide, hydrogen, and other gases.

A STUDY OF THE MIXED HALIDES AND HALO-THIOCYANATES OF LEAD.

By Charles H. Herty and T. R. Boggs.

Received August 24, 1897.

IT has recently been shown[1] by one of us (Herty) that the so-called compound $Pb\langle^{I}_{Cl}$ is not a true chemical compound, but a mixture of lead chloride and lead iodide. More recently Herty and Smith[2] have confirmed McMurtry's[3] observation that the substance $Hg\langle^{Cl}_{CNS}$ is a true chemical compound, and not a mixture of mercuric chloride and mercuric thiocyanate. This suggested the question, Is the formation of mixed crystals in the one case and a true chemical compound in the other due to the character of the metal present or to the difference in the character of the negative radicals present in each case? To determine this a systematic investigation of the products formed by dissolving lead chloride and lead thiocyanate was undertaken. It has been found that $Pb\langle^{Cl}_{CNS}$ is a true chemical compound, just as in the case of $Hg\langle^{Cl}_{CNS}$. Plainly, the character of the metal present is not the determining factor. If then, the difference be due to the character of the negative radicals present, the so-called salt $Hg\langle^{I}_{Cl}$ should be a mixture and not a true chemical compound.

However, before beginning work on this point, it has been deemed advisable to make a thorough study of the compounds of lead with the halogens and with thiocyanogen, including all

[1] *Am. Chem. J.*, **18**, 293.
[2] This Journal, **18**, 906.
[3] *J. Chem. Soc.*, *1889*, 50.

possible combinations of these. In this way the following have been studied:

Lead chloride with lead bromide.
" " " " iodide.
" bromide " " "
" chloride " " thiocyanate.
" bromide " " "
" iodide " " "

In each case seven solutions in water have been prepared, all containing the same weight of lead, but varying proportions of the acid radicals. The middle solution in each series contained the salts in centi-molecular proportions. In the other members of each series arbitrarily taken quantities of one substance were replaced by equivalent quantities of the other substance.

The hot solutions were allowed to crystallize and the crystals thus obtained were dried by pressing between folds of drying paper. The mother-liquors from the first crops were evaporated to two-thirds original volume, and a second crop of crystals obtained. Finally the mother-liquors from the second crops were allowed to evaporate to dryness spontaneously, giving thus a third crop of crystals. Each crop was carefully examined with the microscope to determine its homogeneity. The work is as yet incomplete, but sufficient results have been obtained to justify a description of the work to date.

I. LEAD CHLORIDE AND LEAD BROMIDE.

These two compounds are isomorphous, and we would naturally expect mixtures containing varying proportions of the ingredients. Such have been found. The effect of light upon these crystal masses is worthy of note. Wells[1] and Norris[2] have already called attention to the fact that lead bromide is darkened on exposure to light. So in these mixed crystals, this property of lead bromide is retained, the amount of darkening depending on the proportion of lead bromide in the mixed crystal.

II. LEAD BROMIDE AND LEAD IODIDE.

Only four solutions were here prepared, beginning with the

[1] *Am. J. Sci.*, 45, 134.
[2] *Am. Chem. J.*, 17, 189.

centi-molecular proportion and replacing portions of lead iodide by equivalent quantities of lead bromide.

In each case crystals of lead iodide alone separated as the first crop, even where the proportion of lead bromide to lead iodide was three and one-half grams to two-tenths gram.

The second crops of crystals, however, were prismatic, resembling, somewhat, lead bromide. These crystals show the presence of both bromine and iodine. The color of the respective crops varies from a greenish-yellow to a light sulphur-yellow. All are darkened by exposure to light. The crops are homogeneous. While no analyses have yet been made it is evident that these crystals are mixtures of lead bromide and lead iodide, in which the lead bromide is largely in excess.

Further, a crystal of lead iodide placed in a cold saturated solution of lead bromide is very gradually changed as the solution evaporates spontaneously and finally disappears, the mass being composed, at dryness, of prismatic, faint yellow crystals. This shows the ability of lead iodide to mix in very small quantities with lead bromide.

III. LEAD CHLORIDE AND LEAD IODIDE.

Results already published show that these two substances form mixed crystals, but with lead chloride always present in excess. Engelhardt[1] has also shown that lead iodide and lead chloride can form mixed crystals.

A crystal of lead iodide placed in a cold saturated solution of lead chloride begins to change almost immediately. Examined under a microscope the bright yellow hexagonal plate is seen to grow dark, and soon the crystal is seen to break into prismatic crystals of very slight color.

This can be shown on a larger scale by dissolving three and one-half grams lead chloride and 2.4869 grams lead iodide in 350 cc. hot water. On cooling, crystals of lead iodide separate in large quantities. On standing over night in contact with the mother-liquor all of these crystals are changed to yellowish-green prismatic crystals.

All of the evidence thus far obtained tends to show that lead

[1] *Chem. Centrbl.*, 1855, 817.

iodide and lead chloride will crystallize together, the lead chloride being present in excess.

If we consider such substances as instances of solid solution, the results show that lead iodide dissolves in lead chloride to a greater extent than in lead bromide.

IV. LEAD CHLORIDE AND LEAD THIOCYANATE.

A microscopic examination of the twenty-one crops of crystals obtained in this series showed three substances present, either singly or crystallizing singly side by side, lead thiocyanate, lead chloride, and a new salt, the lead chloro-thiocyanate, formed from the solution containing the ingredients present in centimolecular proportions. There is no evidence of the formation of any mixed crystals.

V. LEAD BROMIDE AND LEAD THIOCYANATE.

The results in this series are exactly analogous to those obtained in IV. Chemical union takes place between the lead bromide and lead thiocyanate.

VI. LEAD IODIDE AND LEAD THIOCYANATE.

In this series no evidence was obtained of the formation either of a chemical compound or of mixed crystals. In every case it was observed that the two original salts crystallized side by side, each retaining all of its properties.

SUMMARY.

Lead chloride with lead bromide forms isomorphous mixtures in all proportions.

Lead chloride with lead iodide forms mixed crystals, always excess of lead chloride.

Lead chloride with lead thiocyanate forms a true chemical compound.

Lead bromide with lead chloride forms isomorphous mixtures in all proportions.

Lead bromide with lead iodide forms mixed crystals, always large excess of lead bromide.

Lead bromide with lead thiocyanate forms a true chemical compound.

Lead iodide with lead chloride forms mixed crystals, chloride in excess.

Lead iodide with lead bromide forms mixed crystals, bromide in large excess.

Lead iodide with lead thiocyanate forms neither mixed crystal nor true chemical compound.

Lead thiocyanate with lead chloride forms a true chemical compound.

Lead thiocyanate with lead bromide forms a true chemical compound.

Lead thiocyanate with lead iodide forms neither a compound nor mixed crystals.

These results can be summarized more suggestively thus:

$PbCl_2$ and $PbBr_2$. Form isomorphous mixtures in all proportions.	$PbBr_2$ and PbI_2. Form mixed crystals. The bromide always in excess.	$PbCl_2$ and PbI_2. Form mixed crystals. The chloride always in excess.
$PbCl_2$ and $Pb(CNS)_2$. Form a true chemical compound.	$PbBr_2$ and $Pb(CNS)_2$. Form a true chemical compound.	PbI_2 and $Pb(CNS)_2$. Form neither mixed crystals nor a chemical compound.

What is the explanation of these phenomena? Several lines of thought suggest themselves:

1. The relative solubilities of the individual substances.
2. The crystal form of the constituents.
3. The electro-potential character of the negative radicals.
4. The amount of dissociation in solution.

It is probable that the explanation is to be found, not alone in any one of the above suggestions, but in several. At the present it is not safe to draw any conclusions or make any generalizations, for there are still a considerable number of facts to be supplied. The work is being carried on as rapidly as possible, and it is hoped soon to have sufficient definite information to throw some light on the question of "chemical compound or mixed crystals."

A series of investigations on mercuric salts is now being carried on in this laboratory analogous to the work on the lead salts. The evidence from this may throw still more light on the question.

UNIVERSITY OF GEORGIA,
July 17, 1897.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE.]

DERIVATIVES OF EUGENOL.

BY F. J. POND AND F. T. BEERS.

Received June 29, 1897.

THE two classes of unsaturated benzene derivatives having the general formulas,

I. $R—CH=CH—CH_3$ and

II. $R—CH_2—CH=CH_2$,

contain the unsaturated group C_3H_5 joined to a benzene nucleus. In the first class of compounds the C_3H_5 group has a propenyl, in the second an allyl structure.

The study of these bodies has been especially directed towards finding a suitable reaction by means of which the character of the unsaturated group might be definitely determined.

The results obtained by the action of nitrogen trioxide on anethol, described by P. Toennies,[1] and those of A. Angeli,[2] embracing the action of the same reagent on eugenol, isoeugenol, safrol, isosafrol, apiol, and isoapiol, led Angeli to give the following classification to these bodies :[3]

I.

Anethol $C_6H_4\begin{cases}OCH_3\\CH=CH—CH_3\end{cases}$

Isoeugenol, $C_6H_3\begin{cases}OCH_3\\OH\\CH=CH—CH_3\end{cases}$

Isomethyleugenol, $C_6H_3\begin{cases}OCH_3\\OCH_3\\CH=CH—CH_3\end{cases}$

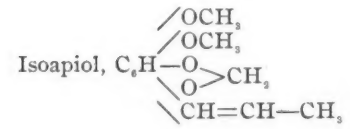
Isoethyleugenol, $C_6H_3\begin{cases}OCH_3\\OC_2H_5\\CH=CH—CH_3\end{cases}$

Isosafrol, $C_6H_3\begin{cases}O\\O>CH_2\\CH=CH—CH_3\end{cases}$

1 *Ber. d. chem. Ges.*, 11, 1511 ; 13, 1845 ; 18, 850 ; 20, 2982.

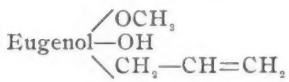
2 *Gazz. chim. ital.*, 22 (II), 445 ; *Ber. d. chem. Ges.*, 24, 3996.

3 *Ber. d. chem. Ges.*, 24, 3994.

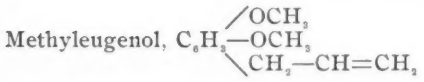


Isoapiol, $C_6H(OCH_3)_2(O_2CH_2)(CH=CH-CH_3)$

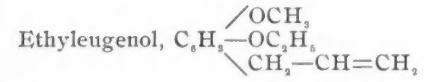
II.



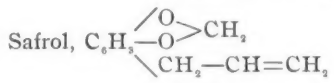
Eugenol—OH, $CH_2-CH=CH_2$



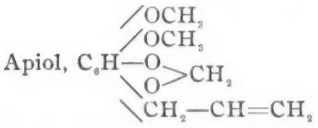
Methyleugenol, $C_6H_3(OCH_3)_2(OCH_3)(CH_2-CH=CH_2)$



Ethyleugenol, $C_6H_3(OCH_3)(OC_2H_5)(CH_2-CH=CH_2)$



Safrol, $C_6H_3(O_2CH_2)(CH_2-CH=CH_2)$



Apiol, $C_6H(OCH_3)_2(O_2CH_2)(CH_2-CH=CH_2)$

All members of the first group were said to give nitrosites when treated with nitrous anhydride, while those in the second class did not. Hence it was assumed that one of the properties which the compounds with a propenyl side chain possessed was to form these addition-products with nitrogen trioxide, which could not be obtained from the allyl side chain bodies.

Later, however, Angeli[1] was able to prepare similar addition-products from the compounds containing the allyl group, and the reaction therefore could not be called characteristic for the propenyl series.

During the study of the action of sodium alcoholate on the bromine addition-products of these two classes of compounds, Wallach and Pond[2] found that some of the propenyl series gave dibromides, which, on treatment with sodium alcoholate, yielded ketones having the general formula

[1] *Ber. d. chem. Ges.*, **26**, Ref. 195.

[2] *Ber. d. chem. Ges.*, **28**, 2714; also Pond, Inaug. Diss., Goettingen, 1896.

$$R—CO—CH_2—CH_3,$$

while the bromine products of the corresponding allyl series, treated in precisely the same manner, gave no ketones, but were, partially at least, changed back into the original compounds. This reaction, which was carried out with anethol, safrol, and isosafrol, eugenol and isoethyleugenol, seemed to give reasonable ground for the belief that it might prove a characteristic reaction, by means of which the nature of the side chain in these two classes of unsaturated bodies could be determined.

The formulation of the reaction of sodium methylate on anethol dibromide (anethol being taken as an example of the propenyl compounds) is the following:

$$C_6H_4\begin{cases}OCH_3\\CHBr—CHBr—CH_3\end{cases} + NaOCH_3 =$$
$$HBr + NaBr + C_6H_4\begin{cases}OCH_3\\C(OCH_3)=CH—CH_3.\end{cases}$$

$$C_6H_4\begin{cases}OCH_3\\C(OCH_3)=CH—CH_3\end{cases} + H_2O =$$
$$CH_3OH + C_6H_4\begin{cases}OCH_3\\C(OH)=CH—CH_3.\end{cases}$$

$$C_6H_4\begin{cases}OCH_3\\C(OH)=CH—CH_3\end{cases} = C_6H_4\begin{cases}OCH_3\\CO—CH_2—CH_3.\end{cases}$$

The alcoholate splits off one molecule of hydrobromic acid from the dibromide in the normal manner, while the second bromine atom suffers replacement by the OCH_3 group. The latter is easily saponified and the resulting unsaturated alcohol, following the Erlenmeyer hypothesis, changes into the more stable saturated ketone.

Eugenol, which was taken as a fair illustration of the allyl series, gave a liquid dibromide, which, on treatment with sodium alcoholate, simply parted with the two bromine atoms, yielding no characteristic body. Safrol acted in much the same manner, while anethol, isosafrol, and isoethyleugenol dibromides gave well defined ketones. It has seemed to us, therefore, of interest to examine this reaction with some other members of the propenyl series, in order, if possible, to give further support to the results already obtained.

Some ester of isoeugenol seemed to promise well for this pur-

pose, and as ethyl and methyl isoeugenol have both shown themselves to conform to the reaction, the question arose whether an aromatic ester of isoeugenol, as for example, benzyl isoeugenol, would not also form a dibromide which could be changed into a ketone. Our results have fully substantiated the belief that such is the case.

BENZYL EUGENOL, $C_6H_3\begin{cases}OCH_3\\ OCH_2-C_6H_5\\ CH_2-CH=CH_2\end{cases}$.

The general rule for preparing esters of eugenol is to treat the potassium or sodium salt of eugenol with an alkyl bromide or chloride.

In such a manner Cahours[1] obtained the benzoyl, toluyl, and ethyl ester, and Wassermann[2] the methyl and some other esters.

Our method was similar to this and consisted in dissolving thirty grams potassium hydroxide in seventy-five cc. alcohol, in a round-bottomed flask with an upright condenser. Seventy cc. eugenol were added and the whole heated on a water-bath. Fifty-three cc. benzyl chloride were introduced, drop by drop, and the heating continued about three hours, until end of the reaction. The potassium chloride formed was dissolved in water and the heavy oil thrown out separated. An attempt to purify by steam distillation proved of no avail, since the oil is almost non-volatile with steam.

The benzyl eugenol is a dark-colored oil, heavier than water, and after drying over calcium chloride boils at about 235° with decomposition. It also suffers decomposition by vacuum distillation.

ISOBENZYL EUGENOL, $C_6H_3\begin{cases}OCH_3\\ OCH_2-C_6H_5\\ CH=CH-CH_3\end{cases}$.

This propenyl compound was easily prepared from the benzyl eugenol according to the general method of Eykman[3] and Angeli[4] by heating with an alcoholic potassium hydroxide solution.

One hundred and fifty grams potassium hydroxide, 300 cc. alcohol, and seventy-five grams benzyl eugenol were heated on

[1] *Ann. Chem.* (Liebig), **46**, 220; **108**, 320.
[2] *Ann. Chem.* (Liebig), **179**, 375.
[3] *Ber. d. chem. Ges.*, **23**, 855.
[4] *Gazz. chim. ital.*, **22**, (2) 101.

a water-bath for about twenty-four hours. After distilling off most of the alcohol the remaining solution was poured into a liter of water, a heavy oil separating, which, after twelve hours standing, solidified. This was filtered, dried on a porous plate, and crystallized from alcohol. The product is at first rather dark-colored and quite impure, hence repeated treatment with animal charcoal is advisable. The substance has the habit of separating from a saturated alcoholic solution as an oil, which slowly solidifies.

When finally crystallized from alcohol, it is perfectly white and in the form of long, fine needles, melting at 48°.

The analyses gave the following results :

I. 0.1858 gram gave 0.5429 gram carbon dioxide and 0.1138 gram water.

II. 0.1804 gram gave 0.5289 gram carbon dioxide and 0.1113 gram water.

	Calculated for $C_6H_3\begin{cases}OCH_3\\OCH_2C_6H_5\\CH=CH-CH_3\end{cases}$.	Found. I.	II.
Carbon	80.31	80.13	79.94
Hydrogen	7.08	6.80	6.85

ISOBENZYL EUGENOL DIBROMIDE, $C_6H_3\begin{cases}OCH_3\\OCH_2-C_6H_5\\CHBr-CHBr-CH_3\end{cases}$.

Twenty-five grams isobenzyl eugenol was dissolved in 100 cc. dry ether and after cooling with a mixture of ice and salt, five and four-tenths cc. bromine (one molecule) were added very slowly. The last drops gave the liquid a permanent yellow color, and at the same time a mass of fine white crystals appeared. These were filtered, washed with cold ether to remove excess of bromine, dried, and crystallized from alcohol. A second crop may be obtained from the ether filtrate by washing with a solution of sulphur dioxide to remove bromine, and evaporating the ether. It crystallizes in white needles melting at 122°, easily soluble in alcohol, more difficultly soluble in ether.

No evolution of hydrobromic acid was noticed either during the addition of bromine or on crystallization.

TREATMENT OF ISOBENZYL EUGENOL DIBROMIDE WITH SODIUM METHYLATE. KETONE, $C_6H_3\begin{cases}OCH_3\\OCH_2-C_6H_5\\CO-CH_2-CH_3\end{cases}$.

To a solution of sodium methylate, formed by dissolving five grams of sodium in 100 cc. methyl alcohol, twenty-six grams of isobenzyl eugenol dibromide were added. A violent reaction at once took place with formation of considerable sodium bromide. The solution was heated with an upright cooler, in a water-bath for about three hours. On addition of water a dark-colored, heavy oil separated, which, owing to being difficultly driven over with steam, was removed by a separating funnel. The oil was then boiled for a short time with a dilute solution of potassium hydroxide to insure a complete saponification of the unsaturated ester, *viz.*:

$$R-C(OCH_3)=CH-CH_3,$$

and then allowed to stand twenty-four hours. At the end of this time a solid appeared, and after three days nearly all the oil had changed into the white solid. The latter was filtered by suction, pressed on a plate to remove any adhering oil, and crystallized from ether in small, white needles melting at 93°.

The analyses gave the figures:

I. 0.2282 gram substance gave 0.6306 gram carbon dioxide and 0.1389 gram water.

II. 0.2251 gram substance gave 0.6216 gram carbon dioxide and 0.1354 gram water.

	Calculated for $C_6H_3\begin{cases}OCH_3\\OCH_2-C_6H_5\\CO-CH_2-CH_3\end{cases}$.	Found. I.	Found. II.
Carbon	75.55	75.32	75.31
Hydrogen	6.66	6.85	6.68

If the substance actually is a ketone it should naturally be converted into an oxime by treatment with hydroxylamine.

OXIME, $C_6H_3\begin{cases}OCH_3\\OCH_2-C_6H_5\\C(NOH)-CH_2-CH_3\end{cases}$.

Fifteen grams of the ketone were dissolved in fifty cc. alcohol, heated to boiling, and a hot solution of fifteen grams hydroxylamine hydrochloride in thirty cc. water added. To this solution fifteen grams potassium hydroxide in fifteen cc. water were

slowly added, care being taken to shake well after each addition. On cooling, the whole was poured into ice water, a white, crystalline precipitate being thrown out. After filtering and drying it crystallized from alcohol, yielding beautiful white needles which melt at 118.5°.

Analyses gave the following :

I. 0.1529 gram gave 0.4024 gram carbon dioxide and 0.0886 gram water.

II. 0.1946 gram gave 0.5116 gram carbon dioxide and 0.1120 gram water.

	Calculated for $C_6H_3\begin{cases}OCH_3\\OCH_2-C_6H_5\\C(NOH)-CH_2-CH_3\end{cases}$	Found. I.	Found. II.
Carbon	71.58	71.77	71.69
Hydrogen	6.66	6.43	6.39

There can therefore be no doubt but that the substance obtained from isobenzyl eugenol dibromide by the action of sodium methylate, consists of a ketone mixed with some unsaturated alcohol or ether, the latter being saponified and changed into the ketone structure on heating with potassium hydroxide or with a dilute mineral acid, as was later found to be the case.

The oxime is easily changed back into the ketone melting at 93°, by heating with dilute sulphuric acid.

That the carbonyl group in the ketone occupies the α- position to the benzene nucleus,

(1) $R-CO-CH_2-CH_3$,

and not β-

(2) $R-CH_2-CO-CH_3$,

has been proved in all this series of ketones by the action of concentrated sulphuric acid on both the ketone and the corresponding oxime, by which propionic acid and not acetic acid results, thus allowing only formula 1.

Isobenzyl eugenol acts thus in a very similar manner to isoethyl eugenol, and adds one more to the list of bodies containing the unsaturated propenyl side chain, whose bromine addition-products may be used as a starting-point for the formation of ketones. It further supports the belief that this reaction may be used to characterize the atomic grouping in the side chain.

Experiments are now under way in this laboratory on eugenol acetic acid and isoeugenol acetic acid, apiol and isoapiol, from which we hope to secure some satisfactory results.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

LIII.—ON THE EXISTENCE OF ORTHOSILICIC ACID.

BY T. H. NORTON AND D. M. ROTH.

Received August 27, 1897.

A NUMBER of attempts have been made to ascertain whether silica combined with water to form a sharply-defined meta- or orthosilicic acid, and hitherto the results have been very nearly as fruitless as those undertaken to isolate the corresponding carbonic acids. Nearly all experiments in this field have been in the direction of determining the water remaining in combination with silica after the precipitated hydrate has been kept in an air-bath at 100°, or in a desiccator over dehydrating substances.

Doveri,[1] the pioneer in this subject, found 17 to 17.8 per cent. water in the air-dried powder—source not given. Maschke,[2] using the hydrate precipitated from alkaline silicates by hydrochloric acid, found from 11.6 to 14.4 per cent. Fuchs,[3] Merz[4] and Gottlieb[5] analyzed the hydrate obtained by the action of water on silicon tetrafluoride. Fuchs found 9.3 per cent. water in a sample dried thirty days over sulphuric acid, and 6.75 per cent. in a sample dried eighteen days at 100°. Merz found for the same 8.66 per cent. and 6.31 per cent. respectively. Gottlieb, whose experiments were made with the greatest care, found 6.13 per cent. water after desiccation over sulphuric acid for 131 days and 4.47 per cent. water after desiccation at 100°. His results point to the formulas $H_4Si_9O_{20}$ and $H_4Si_{13}O_{28}$. He concludes, "from these few determinations we may say with certainty that the compound known as orthosilicic acid, having the formula H_4SiO_4 does not exist any more than the so-called metasilicic acid H_2SiO_3, as the former requires 37.5 per cent., and the latter 23.07 per cent. water, while even an air-dried silicic acid does not contain the latter amount." Rammelsberg[6] says "Gottlieb found 6.13 per cent. water in the acid dried over sulphuric acid, and 4.50 per cent. water in that dried at 100°–140°. I found in the first case, without any special precautions, 4.50 per

1 *Ann. chim. phys.*, [3], **21**, 40.
2 *Pogg. Ann.*, **156**, 90.
3 *Ann. chem.* (Liebig), **82**, 577.
4 *J. prakt. chem.*, **99**, 177.
5 *J. prakt. chem.* [2], **6**, 185.
6 *Ber. d. chem. Ges.*, **5**, 1007.

cent., in the second 4.00 to 5.00 per cent. water. We accordingly have to deal with hydrates $nSiO_2 + H_2O$, where n lies between four and eight. Air-dried silicic acid, as one may be easily convinced, contains no certain amount of water. In the dry powder is found from thirty-six to thirteen per cent. water. The former amount would indicate the formula $SiO_2 + 2Aq$, the latter $2SiO_2 + Aq$. Between these, the figures 23 and 16 per cent. are the most frequent, that is, hydrates $SiO_2 + Aq$ and $3SiO_2 + Aq$.'' Other results, equally varying, will be found in the work of Lippert, of Frémy,[1] who used silicon sulphide, of Ebelmen,[2] who used ethyl silicate, Graham,[3] who employed dialysis, Langlois,[4] who used silicon chloride, Fullik,[5] Carnelly and Walker,[6] and Van Bemmelen.[7] The latter made an especially exhaustive study of the hydrates obtained from different sources and dried in air saturated with moisture, claiming that as many as four molecules of water would be held in combination under these circumstances, the powder still being dry to the touch.

In order to decide the question, we devised the following method of isolating the hydrate, which led conclusively to the establishment of the formula H_4SiO_4 as representing the composition of silicic acid when freshly precipitated, and rapidly freed from adherent water. This was accomplished briefly by washing the moist hydrate with ether or benzene, and removing the latter by pressure between sheets of bibulous paper.

In detail, the following procedure led to the best results : Silicic acid was precipitated by passing silicon tetrafluoride into water. For obvious reasons this is the simplest method of obtaining the compound free from non-volatile foreign matter. The gelatinous mass was thrown upon a cloth filter, washed with water, and allowed to drain a short time. The water was then removed by successive washings with absolute ether or benzene. Usually 150 to 200 cc. were used in an operation. The washed acid was next wrapped in fine cloth, placed between several thicknesses of heavy filter paper and exposed to strong pressure

[1] *Ann. chim. phys.* [3], **38**, 327.
[2] *Ann. chim. phys.* [3], **16**, 129.
[3] *Ann. Chem.* (Liebig), **121**, 1.
[4] *Ann. chim. phys.* [3], **52**, 331.
[5] *Ber. d. chem. Ges.*, *1878*, 2121.
[6] *J. Chem. Soc.*, **53**, 81.
[7] *Ber. d. chem. Ges.*, **11**, 2232 ; **13**, 1467 : *Rec. trav. chim.*, **7**, 69.

in a vise. After several changes of the paper, and absorption had apparently ceased, the cloth was changed, and the operation repeated. The cake was then removed from the cloth, enclosed in gray filter-paper and pressed again. (Cloth was necessary at first on account of the adherence of paper to the acid, and at the end ordinary coarse gray filter-paper was less torn than the customary white paper.) At this stage the cake was nearly dry. It was broken up, powdered and pressed between paper and porous tiles several times, until all traces of moisture had disappeared. This point was easily detected by the eye. A portion of the perfectly dry mass, which amounted ordinarily to ten grams at this stage, was transferred to closed watch glasses, and from these weighed off into a platinum crucible. After ignition the amount of silica present and the consequent loss of water, were determined. About forty-five minutes elapsed usually between the beginning of the operation of pressing and the weighing of the sample for analysis. After a little practice it is possible to detect easily the point of disappearance of all moisture, of whatever nature, which is mechanically present. No time is lost at this stage in taking the sample to check the composition, as the loss of chemically combined water begins at once, and its rapidity is dependent only upon prevailing hygroscopic conditions.

The following determinations of orthosilicic acid, as prepared above, were made. Benzene was employed for the washing in Nos. 9, 10, and 11; in all other cases absolute ether was used. H_4SiO_4 should lose, theoretically, 37.5 per cent. of water.

No.	Weight of sample. Gram.	Water lost. Weight. Gram.	Water lost. Per cent.	Ratio of water to silica.
1.....	0.115	0.0428	37.30	1.97 : 1
2.....	0.2884	0.1054	36.55	1.92 : 1
3.....	0.2826	0.1046	37.02	1.96 : 1
4.....	0.1760	0.0660	37.50	2.00 : 1
5.....	0.3560	0.1370	38.48	2.08 : 1
6.....	0.3642	0.1348	37.01	1.96 : 1
7.....	0.2943	0.1098	37.31	1.98 : 1
8.....	0.2948	0.1098	37.25	1.98 : 1
9.....	0.2473	0.0963	36.50	1.92 : 1
10.....	0.2368	0.0873	36.60	1.92 : 1
11.....	0.1497	0.0562	37.54	2.00 : 1

As was shown by experiment, absolute alcohol could not be used in place of ether or benzene. Its affinity for water is much stronger than that of silicon dioxide, and dehydration began long before the removal of the water mechanically present.

Orthosilicic acid, as obtained above, is an amorphous white powder, perfectly dry to the touch, which may be preserved indefinitely in hermetically closed vessels, but loses its water of hydration steadily on exposure to the air, and especially when in contact with absorbent media.

As examples of this latter property the following analyses were made of (A) samples taken from cakes just dried, and (B) of samples taken from the same cakes, after being pressed for five to ten minutes longer between sheets of filter paper.

	Water.	
No.	A.	B.
	Per cent.	Per cent.
1	37.02	37.01
2	37.50	37.30
3	38.02	34.42
4	37.01	36.95
5	37.31	33.30
6	36.50	36.40
7	36.60	36.10
8	37.50	36.40

It is probable that in all our experiments a slight loss of water of hydration occurred before the ether or benzene was completely removed by contact with bibulous paper, as the average of the analytical results is slightly below the theoretical figure, 37.5.

The existence of the orthosilicic acid as a definite body may be therefore considered as established.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

LIV.—DERIVATIVES OF BENZENESULPHONIC ACID.

BY T. H. NORTON.

Received August 27, 1897.

IN connection with a general study of the derivatives of benzenesulphonic acid,[1] carried on in this laboratory, the material for the two following notes was collected.

PREPARATION OF BENZENESULPHONIC BROMIDE.

The only recorded method of preparing the substance is that

[1] Norton and Schmidt: *Am. Chem. J.*, 10, 136; Norton and Westenhoff: *Ibid*, 10, 129.

given by the discoverer, Otto,[1] and consists in warming together bromine and benzenesulphinic acid. As the preparation of the latter compound involves the use of benzenesulphonic chloride, it seemed desirable to devise a shorter and simpler method for obtaining the bromide, as well as to determine some of its constants. In looking over the brief list, as given in Beilstein's Organic Chemistry, of sulphonic bromides thus far known, most of which we owe to Otto, it will be seen that the corresponding sulphinic acid is almost unvariably used. Experiment showed that satisfactory results could be obtained by treating dry sodium benzenesulphonate with phosphorus pentabromide. The latter was employed either in the solid form or dissolved in carbon disulphide. The former method gave the best yield. In either case the perfectly dry sulphonate was well rubbed in a mortar with the pentabromide. Considerable heat was involved. On adding the product to water, the benzenesulphonic bromide, $C_6H_5SO_2Br$, separated out in the form of a heavy liquid, colored red from free bromine. It was well washed with water, and dried in contact with calcium chloride. Several preparations were made, but in no case was the yield over one quarter of the theoretical.

Thus prepared, the bromide is a colorless liquid, frequently with a faint reddish tinge, of an oily appearance, with a sharp penetrating odor. Its specific gravity is 1.693 at 21°. It distils at 140°-141° (uncor.) with slight decomposition.

An analysis by Carius' method gave:

	Found.	Theory.
Bromine.....	35.02	36.20

BENZENESULPHONATES OF THE ALKALINE METALS.

Although two of these salts are used technically, none of them have been subjected to careful analysis or examination.

Sodium Benzenesulphonate, $C_6H_5SO_3Na$. This salt was prepared by adding an aqueous solution of sodium carbonate to an aqueous solution of barium benzenesulphonate until the point was exactly reached, at which no further precipitate was formed. The filtered solution of the sodium benzenesulphonate was evaporated to the point of crystallization. It crystallizes in the form of small, white, anhydrous leaflets. It melts with some decomposi-

[1] Otto: *Ann. Chem.* (Liebig), **341**, 373.

tion at about 450°. It is insoluble in ether and benzene, and but slightly soluble in alcohol. It dissolves in 1.75 parts of water at 30° and in 0.8 part of boiling water.

Analysis.—The salt dried to constant weight over sulphuric acid *in vacuo*, lost no weight on heating to 135°.

0.3624 gram of the dried salt gave 0.1423 gram Na_2SO_4 = 0.046 gram Na = 12.72 per cent.

	Theory.	Found.
Sodium	12.77	12.72

Potassium Benzenesulphonate, $C_6H_5SO_3K$.—This salt was prepared in the same way as the sodium salt, potassium carbonate being used. It crystallizes ordinarily in long, delicate, colorless needles, with a silky luster, united frequently in radiated clusters. Long flat prisms are obtained by very slow evaporation. The salt is anhydrous and melts at about 408°. It is insoluble in ether and benzene, and nearly insoluble in alcohol. It dissolves in 0.66 part of water at 30°, and in 0.29 part of boiling water.

Analysis.—The salt dried to constant weight over sulphuric acid *in vacuo*, lost no weight on heating to 115°.

0.2567 gram of the dry salt gave 0.1121 gram potassium sulphate = 0.05 gram potassium = 19.58 per cent.

	Theory.	Found.
Potassium	19.90	19.58

Ammonium Benzenesulphonate, $C_6H_5SO_3NH_4$.—This salt was prepared in a manner similar to those above described, ammonium sulphate being used in the precipitation of the barium salt. Crystals are obtained with difficulty on account of the deliquescent nature of the salt. When prepared in a vacuum, over sulphuric acid, they show a radial structure with pearly luster, but are poorly defined. The salt begins to decompose at 236° and melts at 256°. It is soluble in 1.02 parts of cold water and in 0.31 part of boiling water. It dissolves in five and two-tenths parts of cold alcohol and in three and one-tenth parts of boiling alcohol, but is insoluble in ether and benzene.

Analysis.—The salt dried over sulphuric acid *in vacuo*, lost no weight at 105°.

One-half gram of the dry salt gave by the potassium chlorate

method, 0.652 gram barium sulphate, or 0.0895 gram sulphur = 17.87 per cent.

	Theory.	Found.
Sulphur	18.28	17.87

Lithium Benzenesulphonate, $C_6H_5SO_3Li$.—This salt was prepared in the same way as the sodium salt, lithium carbonate being used. It crystallizes in stellate groups of delicate, white, anhydrous needles. It melts at a dull red heat. It is soluble in 1.02 parts of water at 30°, and in five-tenths part of boiling water, in one and five-tenths parts of cold alcohol, and in nine-tenths part of boiling alcohol. It is insoluble in ether and benzene.

Analysis.—The salt dried over sulphuric acid *in vacuo*, lost no weight at 105°.

0.3032 gram of the dried salt gave 0.1032 gram lithium sulphate, or 0.013 gram lithium = 4.27 per cent.

	Theory.	Found.
Lithium	4.26	4.27

I am indebted to H. C. Buell and H. E. Newman for aid in these determinations.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

LV.—ON A SOLUBLE COMPOUND OF HYDRASTINE WITH MONOCALCIUM PHOSPHATE.

BY T. H. NORTON AND H. E. NEWMAN.

Received August 27, 1897.

THE following experiments were made in connection with an endeavor to enlarge the number of soluble salts of hydrastine, especial interest attaching to the combination of the alkaloid with a mineral salt of recognized value in medicine.

As is well known, but few salts of hydrastine are readily soluble in water. In our work we made use of monocalcium phosphate, which was carefully purified by prolonged washing with alcohol. A saturated solution of the salt in cold water was prepared by thorough trituration, the phosphate being in excess. On triturating this saturated solution with a large excess of pure hydrastine, a certain amount of the latter would enter into solution, time, as was eventually found, being an important factor.

In order to ascertain the nature of the product obtained, the filtered solution was evaporated either by heat or spontaneously, or in a vacuum. In no case was it possible to detect any trace of crystallization. The solution invariably became syrupy, and finally left an amorphous residue quite similar to rosin in its appearance. This residue was soluble in about ten parts of cold water. A small amount of boiling water would change it into a syrup. Both boiling and cold alcohol dissolved it easily and in about the same proportions. The melting-point was 126°–128°. Although there was no criterion of the purity of the substance it was submitted to analysis. No success followed an attempt to determine the amount of hydrastine present by the use of potassium permanganate, as no definite end reaction could be obtained. Resort was then had to incineration, care being taken to avoid unnecessarily high temperatures in the use of platinum dishes for the purpose. The substance dried *in vacuo* was heated to 105°. The very divergent results obtained showed that there was no fixed percentage of water held by the compound after desiccation *in vacuo*. The product of incineration was white, vitreous calcium metaphosphate.[1] It was in all cases calculated to monocalcium orthophosphate, and the difference was assumed to be hydrastine. Analytical results soon showed that prolonged trituration was necessary to increase the amount of the alkaloid taken into combination by the phosphate. From two-tenths to one-half gram was used in each analysis of the substance dried at 105°. The following analytical data were obtained:

No.	Time of trituration.	Monocalcium phosphate. Per cent.	Hydrastine. Per cent.
1	10 minutes	44.69	55.31
2	15 "	38.33	61.67
3	5 "	55.70	44 30
4	3 "	57.73	42.27
5	80 hours[2]	29.00	71.00
6	80 "	28.03	71.97
7	40 "	31.00	69.00
8	50 "	30.43	69.67
9	50 "	28.10	71.90
10	6 weeks	28.95	71.05

[1] Birnbaum: *Jsb. d. Chem.*, *1871*, 281.

[2] In experiments 5-10 the alkaloid and the solution were placed in a corked bottle, and this was introduced into a box provided with paddles and suspended on an axis, which was kept in constant agitation beneath a water tap.

In order to appreciate these figures, let us note the theoretical percentages of the simpler possible combinations of monocalcium phosphate and hydrastine.

A. $2Ca(H_2PO_4)_2.C_{21}H_{21}NO_6$.
$Ca(H_2PO_4)_2 = 54.10$ per cent.
$C_{21}H_{21}NO_6 = 45.90$ per cent.

B. $Ca(H_2PO_4)_2.C_{21}H_{21}NO_6$.
$Ca(H_2PO_4)_2 = 37.9$ per cent.
$C_{21}H_{21}NO_6 = 62.1$ per cent.

C. $2Ca(H_2PO_4)_2.3C_{21}H_{21}NO_6$.
$Ca(H_2PO_4)_2 = 28.9$ per cent.
$C_{21}H_{21}NO_6 = 71.1$ per cent.

It will be seen at once that the apparent limit of the amount of hydrastine which can enter into combination with the phosphate, as shown by analyses 5–10, is practically identical with the percentage of the alkaloid present in the hypothetical salt C, where two molecules of monocalcium phosphate are in combination with three molecules of the alkaloid. In the picrate of hydrastine, one of the few crystalline derivatives, we encounter a combination of equal molecules $[C_6H_2(NO_2)_3OH.C_{21}H_{21}NO_6]$, the amorphous sulphate and chloride ($C_{21}H_{21}NO_6.H_2SO_4$) correspond, however, to the formula B. While the formula C is unsupported by analogy and the aid of crystallization is lacking, the analytical data point strongly towards this as the correct expression for the product obtained by the method described.

TORONTO MEETING OF THE BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

THE British Association for the Advancement of Science met in Toronto, August 18–25. Many prominent scientific men from Canada and the United States, as well as from Great Britain, were in attendance.

Professor William Ramsay, of London, was president of the chemical section. His address was on "An Undiscovered Gas." A consideration of the periodic law and of the atomic weights of helium and argon (4 and 40) suggests that there may be another similar element with an atomic weight of about 20. Helium has been subjected to a long series of diffusions by Pro-

fessor Ramsay and Dr. Collie in the endeavor to find such a substance. The gas was by this means separated into a lighter portion with a density of 1.98 and a heavier portion with a density of 2.275 ($H_2 = 1$). The spectroscopic examination showed the presence of argon in the heavier portion, but no evidence of the existence of a new gas could be discovered. Such a negative result cannot, of course, be taken as proof of the nonexistence of the substance sought, and Professor Ramsay very courteously concluded his address by expressing the hope that the prophecy implied in it may find its fulfilment on this side of the ocean.

The papers of most interest presented before the section were the following:

Professor Ramsay described in detail the apparatus used for the diffusion experiments with helium, and described experiments which demonstrated that the apparatus could be successfully used to separate air into two portions, one richer and the other poorer in oxygen, while nitrogen cannot be so separated into a lighter and a heavier portion.

Professor B. Brauner, of Prague, Austria, read an interesting paper on "The Atomic Weight of Thorium" and demonstrated the use of ammonium oxalate in separating thorium from other rare metals.

Professor T. W. Richards, of Harvard University, gave a short account of his recent determinations of the atomic weights of nickel and cobalt, which show the same painstaking care and accuracy which has been attained in his previous work.

Mr. Ramage, of Dublin, presented a paper by Professor W. N. Hartley and himself on the "Spectroscopic Examination of Minerals and Earths." The paper was illustrated by the projection of photographs of spectra obtained, chiefly, in the oxyhydrogen flame. They have demonstrated the presence of gallium, indium, thallium, and other rare elements in many samples of iron and of iron ores. The presence of gallium, especially, has also been demonstrated from the spectra of the flames of Bessemer converters.

On Monday, Professor Meslans, an associate of Professor Moissan, of Paris, contributed a "Demonstration of the Preparation and Properties of Fluorine." The gas was prepared by the electroly-

sis of anhydrous hydrofluoric acid containing acid potassium fluoride in a copper vessel surrounded with a freezing mixture. To free the gas from vapors of hydrofluoric acid it was passed through a copper coil surrounded with solid carbon dioxide and alcohol. The action of fluorine on charcoal, silicon, sulphur, iodine, potassium iodide, and on various compounds of carbon was demonstrated.

A paper by Professors Moissan and Dewar on the "Properties of Liquid Fluorine" was also read. The boiling-point is —185° to —187°, the critical temperature —118°, the critical pressure twenty-five atmospheres. The density of the liquid fluorine is 1. The gas liquefies in boiling air but not in boiling oxygen. It is soluble in liquid air.

Professor H. B. Dixon, of Manchester, England, read a paper on "Photographs of Explosion Flames." Photographs were projected of explosion flames as taken on sensitive paper attached to a rapidly moving drum. The photographs demonstrate that mixtures of cyanogen with an excess of oxygen burn at first to carbon monoxide, the temperature being probably above the dissociation temperature of carbon dioxide. The velocity of waves in the incandescent gas from mixtures of cyanogen and oxygen, as shown by the photographs, indicates a temperature of 3,000° to 4,000°.

Professor J. U. Nef, of Chicago, read a paper on the Chemistry of Methylene. The preparation and remarkable properties of some newly discovered derivatives of methylene were described. Among the most interesting of the new compounds are the derivatives of acetylidene, $CI_2=C$ and $CHI=C$. In the latter case the isomer $CH=CI$ has also been prepared and exhibits a very remarkable difference in its properties. Dr. Nef appears to consider the preparation of a gaseous carbon of the formula $C=C$ as possible, though, perhaps, scarcely probable.

On Tuesday morning the chemical section met with the sections for physiology and botany to listen to a paper by Professor Meldola, of London, on the Rationale of Chemical Synthesis. About 300 compounds found in plants and animals have been prepared by synthetical processes in the laboratory. The opinion was expressed that most of these compounds are on what may be called a low level, as compared with the most important com-

pounds which are formed synthetically in vegetable and animal cells. The laboratory processes, too, are, as a rule, radically different from the processes within the living forms, though no one now believes that the chemical forces within the organism differ in any respect from those outside. In the discussion which followed, in which several biologists and chemists took part, it appeared to be the general consensus of opinion that very little real knowledge has thus far been gained in regard to the processes which give rise to the synthesis of starch, proteids, and other similar substances within living organisms, and some of the enormous difficulties which prevent, thus far, the successful study of such problems were pointed out.

On Friday evening Professor W. C. Roberts-Austen, of London, gave a lecture on Canada's Metals. The experimental illustrations were striking, though their connection with the subject-matter of the lecture was remote. Among the more notable demonstrations were instantaneous photographs showing the similar phenomena produced by the fall of a bullet into a basin of milk and of a bullet of gold into a plate of gold, the constancy of temperature during the melting or solidification of gold as shown by a thermoelectric couple and galvanometer, and the melting of copper, chromium, and silver in an electric furnace, the phenomena being made visible to a large audience by reflection on a screen by means of a concave mirror.

Other papers presented before the chemical section were:

Prof. W. W. Andrews: Reform in the Teaching of Chemistry.

Dr. J. Waddell: The Permeability of Elements of Low Atomic Weights to the Roentgen Rays.

Dr. J. H. Gladstone and W. Hibbert: Continuation of Experiments on Chemical Constitution and the Absorption of X-Rays.

Dr. W. J. Russell: On the Action Exerted by Certain Metals on a Photographic Plate.

M. Travers: The Occurrence of Hydrogen in Minerals.

Prof. F. P. Dunnington: Titanic Oxide.

Prof. F. P. Dunnington: Deliquescence and Efflorescence of Certain Salts.

Dr. J. Waddell: Notes on Concentrated Solutions of Lithium and Other Salts.

Prof. Ramsay: Demonstration of the Spectra of Helium and Argon.

W. L. T. Addison: The Formation of Crystals.

E. C. C. Baly: A Compound of Ozone and Mercury.

J. W. Walker: The Interaction of Hydrobromic and Bromic Acids.

F. J. Shutt: The Composition of Canadian Virgin Soils.

W. H. Ellis: Analyses of Some Pre-Carboniferous Coals.

Prof. P. C. Freer: The Constitution of Aliphatic Ketones.

Prof. Henry: The Nitroalcohols.

Dr. A. Lehmann: Formation of a Benzene Ring by Reduction.

Dr. C. A. Kohn: Condensation Products of Aldehydes and Amides.

Dr. Hugh Marshall: A New Form of Bunsen Burner.

Prof. W. C. Roberts-Austen: Molecular Movements in Metals.

Prof. W. W. Andrews: The Plaster of Paris Method in Blowpipe Analysis.

Dr. W. L. Miller and T. R. Rosebrough: The Vapor-Tensions of Liquid Mixtures.

Dr. C. A. Kohn: The Electrolytic Determination of Copper and Iron in Oysters. W. A. NOYES.

BOOKS RECEIVED.

Some Common Poisonous Plants. By V. K. Chesnut. [Reprinted from the Yearbook of the Department of Agriculture for 1896.] 10 pp. U. S. Department of Agriculture, Division of Botany, Washington, D. C.

Commercial Fertilizers. By H. A. Huston. Special Bulletin, Second Edition. August, 1897. 8 pp. Published by the author. Lafayette, Ind.

Analyses of Manurial Substances and Licensed Fertilizers collected during 1897. Bulletin No. 48, July, 1897. Hatch Experiment Station of the Massachusetts Agricultural College, Amherst, Mass.

Annali del Laboratorio Chemico Centrale Delle Gabelle. Vol. III. Pubblicati daV ittoria Villavecchia. Roma: Tipografia Nazionale di g. Bertero via Umbria. 1897.

Lettera al Prof. S. Cannizaro; Sopra alcune sostanze che si ricavano dall'olio di sesamo e sulla relazoine che esse hanno con la ieazione cromatica caratteristica di quest'olio; Sopra la composizione delle farine italiane e sui criteri che valgono a caratterizzarle nel commercio; Sul gelsolino; Contributo allo studio delle analisi dei saponi; Sopra i petroli da illuminazione che si consumano in Italia; Sopra la dulcina o parafenetol-carbammide e sul modo di riconoscerla; Sull'analisi dei canditi; Sopra la composizione chimica di alcuni vini greci; Recerche sui dégras; Sulla determinazione della glicerina nei vini dolci.